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HISTORICAL CLIMATOLOGY

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R and D Associates

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A methodology for evaluation of past climates in historic times has been examined from a theoretical basis and its evaluation has been initiated. The principle is that the ratios of stable isotopes in a tree depend on the temperature at which its wood is manufactured as well as on the temperature at which precipitation, which nourishes the tree is produced. By measuring stable isotope ratios in a chronological sequence of dated tree rings, changes in climate may be evaluated. A tree has been so measured for the years 1700-1950

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95

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Block 20. Abstract (Continued)

and compared with the thermometer record for those years to obtain phenomenological (numerical) temperature coefficients for the ratios of hydrogen, carbon, and oxygen. A second tree has been measured for the years 1500–1800 and found to show the low temperatures of the Little Ice Age with warm brief intervals at about 1570, 1650, 1730 and 1790. A theoretical study of various aspects of the total carbon inventory on the earth's surface has been initiated.

TABLE OF CONTENTS

SECTION 1. RESEARCH PROGRAM

Mechanical thermometers were invented about 1680 A.D. The records of temperature for the next 50 years or so are difficult to correlate with each other, however, because the calibrations differed from thermometer to thermometer. Nevertheless, heroic efforts have been made to do so, and thus the record of the long, slow increase in air temperature since the Little Ice Age has been unraveled. If one wishes to study climate changes before this time it is necessary to invent and calibrate other kinds of thermometers.

Some 25 years ago Harold Urey made the first attempt by measuring the isotope effect in the carbonate of shells, that is, the variation of the ratio of C^{13}/C^{12} or O^{18}/O^{16} in shells grown in water of different temperatures. (The values of the ratio are larger at higher temperature.) However, in order to evaluate the water temperature in which the shell grew, it is necessary to know the isotope ratios in the water and in the carbonate-bicarbonate ion where the shell grew. Since in general these are not known for old shells, the isotope thermometer in shells has not been very useful. Furthermore, this method provides only one thermometer, because carbon and oxygen are bound through the same force constant k, and therefore vibrate against each other with the same frequency, ω. Since the isotope ratio depends only on $\hbar\omega/kT$, the temperature effects on carbon and on oxygen are proportional to each other and hence give redundant information.

In the present research, the isotope thermometers in bio-organic material are being calibrated. Here there are five independent thermometers, namely hydrogen, carbon, nitrogen, oxygen and sulfur.

Any given one of these temperature coefficients should have the same numerical value in all bio-organic materials because its bonds have about the same strengths in all bio-organic molecules. If parallel changes are observed in two or more of these thermometers in stored bio-organic material from past times, it becomes increasingly likely that a climate change is the cause. Accordingly, this research program became oriented toward measuring temperature coefficients of bio-organic material both in general situations where atmospheric CO_2 (which has the same isotopic composition world wide) and rain water are involved, and also in special fresh-water environments. The ramifications and applications appear to be large.

At present, the climate of the northern hemisphere appears to be in a long-term decline that began in 1935. Accompanying the decline in temperature have been 50 year droughts in Japan, North Africa, India, South America and the Mediterranean. Indicative of this trend is a statement, by the head of the Soviet weather service, Dr. Yevgeny K. Federov quoted in the New York Times that temperatures in 1972 in central Russia were the lowest in several hundred years. If the temperature decline and the long-term droughts persist the effect on world food supply could become critical. In illustration of the recent rapid decrease in world food reserves, is an estimate of Lester R. Brown, Overseas Development Council, New York Times, January 26, 1974, of reserves for 95 days in 1961, for 51 days in 1971, and for 29 days in January 1974. This estimate presumably takes into account the increase in world population of about 30% during the interval.

The food shortage is likely to be enhanced by the fuel shortage because this has produced a shortage of fertilizer on which the new "Green Revolution" high yield grains are dependent, being unable to thrive on old-fashioned animal manures.

2

The present research program may succeed in developing a method to
evaluate temperature trends in the historic past, say for the last
10,000 years, and from the record to determine the pattern of climate
changes, from which we may be able to better predict the climate changes
to be expected in the near term and their potential impact on food
supply.

SECTION 2. MAJOR ACCOMPLISHMENTS

The following references and abstracts describe the studies performed under this contract.

"Measurement of O^{18}/O^{16} by Neutron Activation," by R. G. Jackson, L. M. Libby, and H. R. Lukens, J. Geophys. Res., 78, p. 7145 (1973). (See Appendix A.)

The commercially available services for isotope measurement of an accuracy useful in evaluation of past climates from bio-organic material are exceedingly limited. In seeking to alleviate this shortcoming, and in accordance with one of the tasks of this contract, we have proven that the ratio O^{18}/O^{16} can be measured in water using neutron activation to an initial accuracy of a few parts in 10^4, with good prospects of improved accuracy. By a small increase in detector sensitivity the method promises to become of commercial importance.

"Isotope Ratios in a Bristlecone Pine," L. M. Libby and L. J. Pandolfi.

We measured the ratios O^{18}/O^{16} and C^{13}/C^{12} in a piece of bristlecone pine for the years 500 B.C. to 200 A.D., with the intention of comparing them with those of a recent pine grown at the same site (Almagre Mountain, Colorado Springs, Colorado, 11,000 ft altitude). Then we learned by study of the recent pine that each tree ring remained in the sapwood for as long as 90 years, permitting isotope exchange between cellulose and sap over this period and possibly smearing any temperature record over this period. The temperature record made at the site from mercury thermometer readings extends over only the last 90 years. Thus we could not calibrate the observed isotope changes using this record. However, we can say that for both O^{18}/O^{16} and C^{13}/C^{12} ratios the difference between the old pine and the modern pine indicated that the climate was warmer 2000 years ago than now.

The measurements are shown in Table 1. The age of the old tree was determined by radio carbon dating, by Dr. Rainer Berger, UCLA, to a precision of $\pm$60 years. The modern tree rings were dated by Dr. Valmont La Marche, Tree Ring Laboratory, University of Arizona, who cored the tree and courted the rings.

Table 1. Average Ratios in Bristlecone Tree Rings, 1896-1951 A.D. and 550 B.C.-75 A.D.

	(C^{13}/C^{12})*	(O^{18}/O^{16})*	Time Span
Modern	.013062	.0024924	1896-1951 A.D.
Old	.013240	.0025400	550 B.C.-75 A.D.

*With errors of about 0.5 parts per thousand

As shown in Table 1, both isotope ratios are larger in the old tree than in the modern tree. Based on these data, thermodynamic considerations indicate that the old tree grew in a warmer climate. But since there is available no experimental determination of the temperature coefficient for these ratios in Bristlecone pines, we can't say how much warmer. However, if one assumes that the Bristlecone temperature coefficients may be equal to those we have evaluated for the European Spessart Oak, of 4.4 $\pm$0.3 ppt/°C for oxygen and 1.8 $\pm$0.3 ppt/°C for carbon, the difference in the oxygen ratio would indicate a climate colder today by 4.3 $\pm$0.3°C and the carbon difference would indicate 7.6 $\pm$1.4°C colder, for an average climate change of 6.0 $\pm$1.4°C. Nevertheless, there is no reason to believe in the validity of this number, both because temperature coefficients for pines may differ from those for oaks and also because these numerical temperatures coefficients (4.4 and 1.9 ppt per °C) were evaluated from a smaller temperature change, about 1.8 degrees.

5

If the temperature coefficients are not independent of temperature, there may be a substantial error in using them to evaluate a temperature change of several degrees.

It is clear that many new questions have arisen in the course of this research project; it is important to evaluate the answers in order that this potential new field of historic climate determination may become viable.

"Temperature Coefficients of Stable Isotopes Measured in Hot Spring Algae," by L. M. Libby and L. J. Pandolfi, is appended herewith, together with the first page of proof for its publication, (see Appendix B.)

The algae in which isotope ratios were measured grew at various places of successive lower temperatures in the downflow of the famous hot springs of Rotorua, New Zealand. In evaluating the temperature coefficients of the isotope ratios of these algae, we have assumed that the isotopic ratio of the spring water remained unchanged during the flow down hill. To check this point I have written to Dr. Athol Rafter, Director of the Institute of Nuclear Sciences, and to Mr. Thomas Grant-Taylor, Geological Survey, both in the Department of Scientific and Industrial Research, Lower Hutt, New Zealand, asking if they will have the isotope ratios measured in water samples obtained at 60° and at 30° centigrade on the downhill slope or alternatively send me the samples.

"Experimental Determination of Temperature Coefficients of Isotope Ratios in Elodea," by L. M. Libby and L. J. Pandolfi.

The angiosperm Elodea was grown in an outdoor pond, temperature controlled at 10°C and 20°C. The crop of new tips was harvested after about 2 months of growth at each temperature and the C^{13}/C^{12} ratios measured in the

6

material. To effect these measurements, the entire tips were dried in vacuo, and then subjected to chemical treatments for evolution of gases measureable in a mass spectrometer. (See Appendix C.) The data are shown in Table II as well as the experimentally evaluated temperature coefficient.

Table 2. Isotope Ratio Measured in Pond Grown Elodea

Water Temperature	C^{13}/C^{12}	Experimental Temperature Coefficient
4°C	12992 $\pm$43	
10°C	13009 $\pm$38	(0.26 $\pm$ 0.13) ppt/°C
20°C	13053 $\pm$55	

During the course of this experiment, because the pond was outdoors and quite small, 9 cu ft, it was subject to rapid evaporation, so that make-up water had to be added almost every day, from the Los Angeles water supply. The source of the Los Angeles water supply is in part the melting snows of Mammoth, whose isotope ratios vary with the time of year at which the snow is deposited because the air temperature of the snow-clouds is variable. Thus the isotope ratio of the make-up water changed during the experiment as it was produced from the melting snows. On account of this varying and uncontrollable effect, we could not correct the measured oxygen and hydrogen isotope ratios in a reliable way and so can not report our measurements. To evaluate their coefficients will require growing plants under conditions where the make-up water comes from a water tank so enclosed that evaporation cannot occur, and of sufficiently large volume as to last for the duration of the experiment.

7

"Calibration of Isotope Thermometers in a European Oak," L. M. Libby and L. J. Pandolfi, presented at the NSF International CLIMAP Meeting on Climatic Parameters Since 17,000 B.C., May 17-23, 1973, University of East Anglia, Norwich, England, in publication in the Proceedings; and presented at the International Colloquim, C.N.R.S., Centre des Faibles Radioactivite, Oef-sur-Yvette, France, "Quantitative Methods of Study of Climate in the Pleistocene," June 5-8, 1973, and published in the Proceedings (first page of proof appended herewith), further reviewed by Prof. Hans Suess, UCSD (See Appendix C).

We measured the isotope ratios of carbon, hydrogen, and oxygen in rings of a German oak for the years 1710 to 1950 and compared them with measured air temperatures of England, Basil and Geneva for the same time span. In this way, we obtained numerical evaluations of the temperature coefficients of all three isotope ratios.

The isotope ratios have been measured in an oak obtained from Dr. B. Becker, Landwirtschaftliche Hochschule, Universitat Hohenheim, Stuttgart. It was grown in the Spessart mountains in 1514-1850 A.D.: its rings have been cross-dated with the Huber master tree ring chronology by Becker. The measured ratios are shown versus years in Figure 1. The temperature coefficient for C^{13}/C^{12}, as determined by the warm period around 1730, is comparable with that measured for the oak from Munich. However, the coefficients for D/H and O^{18}/O^{16} seem to be only half as large as for the Munich oak, suggesting that this second oak was partly nourished by old ground water which was insensitive to isotope changes in yearly precipitation. However, Becker has no information on the source of water for the second oak. The records for all three indicate that the years 1540-1700 were cold, in agreement with what is known about the Little Ice Age.

I sent the data for this second oak (Figure 1) to Professor H. H. Lamb, Director of the School of Environmental Sciences, University of East Anglia, Norwich, Norfolk, England, for his comments. He replied as follows:

"The C^{13} temperature curve on the Spessart oak looks to me as if it correlates well with the variations of Baltic ice (dates of opening of the port of Riga). All your curves show the interesting warm intervals during the cold ("Little Ice Age") time, viz. mid 1600s, also 1570s, 1730s, 1790s with which I (i.e. my various data) agree."
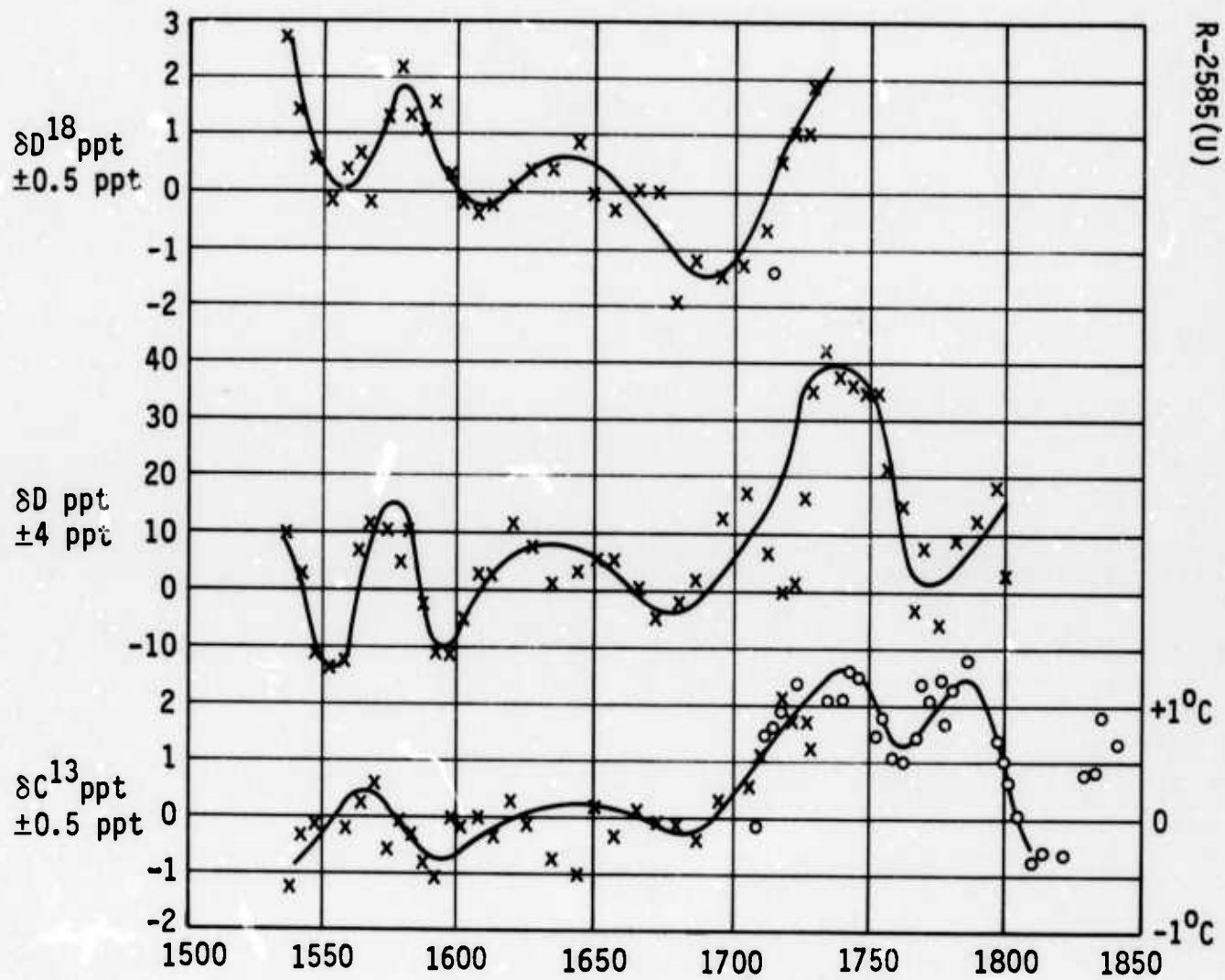
Figure 1. Isotope Ratios Measured in the Second Spessart Oak Plotted Versus Dates Evaluated From Official Tree Ring Analysis.

2.1 CLIMATIC INFLUENCES ON RADIOCARBON DATES

This portion of the research program has the objective to account for the complete carbon inventory and its perturbations. The following reports have been prepared to date:

a) "Vulcanism and Radiocarbon Dates," by L. M. Libby and W. F. Libby, Proceedings of the 9th International Radiocarbon Dating Conference, October 1972, Lower Hutt, New Zealand, ed. T. A. Rafter and T. L. Grant-Taylor, page A72 (See Appendix D).

We compared the amount of CO_2 emitted from volcanoes with the amount of CO_2 being injected into the atmosphere by burning of fossil fuels we are able to conclude that volcanoes cannot cause important perturbations unless they increase in frequency by a factor 100 or more.

b) "Production of Radiocarbon in Tree Rings by Lightningbolts," by L. M. Libby and H. R. Lukens, J. Geophys. Res., 78, p. 5902 (1973) (See Appendix E).

Consideration of neutron production in electric discharge through threads in the laboratory gives an experimental basis for estimating neutron production in lighting discharges. Radio-carbon production in a tree struck by lightning may be measureatle, of order 1%, of the radio carbon produced by cosmic ray neutrons.

c) "Globally Stored Organic Carbon and Radiocarbon Dates," by L. M. Libby, J. Geophys. Res., 78, p. 7667 (1973) (See Appendix F).

11

Using recent data on the rate of addition of CO_2 to the atmosphere by bacteria it is found that variations of climate acting on the biosphere can cause fluctuations of up to ± 100 years correction to radio carbon dates.

12

SECTION 3.   CONCLUSIONS

It is perhaps the basic nature of fundamental research that new problems
arise as a consequence of trying to answer an initial problem. In the
present research a large number of new questions have appeared, such as
1) are the isotope temperature coefficients alike in all European oaks?
2) are other kinds of trees similar to oaks in that respect, in parti-
cular the Bristlecone pines for which there exist chronological sequences
of tree rings for the last 8000 years? and 3) are the temperature
coefficients for isotope fractionation in manufacture of cellulose
and for formation of rainfall separately evaluable? The answer to this
third question is basic to understanding isotope thermometry in trees.
To evaluate these two effects separately we must grow plants under
conditions where both temperature and the isotope ratios of the water
supply are controlled. Under these conditions, the measured temperature
coefficients of the isotope ratios will be those characterizing manu-
facture. The temperature coefficients measured for tree rings in
natural environments are equal to the sum of the coefficient for chemi-
cal manufacture of cellulose plus the coefficient for formation of
precipitation in the troposphere above the tree.

Numerical results to date are summarized in Table III.

Consultants to this project are Prof. Hans Suess and Harmon Craig
(UCSD), V. C. LaMarche and B. Bannister (University of Arizona), R.
Berger, L. Pandolfi and W. F. Libby (UCLA), H. G. Jackson and J. Enstrom
(UCB), and S. Korff (NYU).

Table III

Summary of Temperature Coefficients of Isotope Fractionation in Organic Materials

Temperature Coefficients for Biological Materials (ppt/$^{\circ}$C) Measured for Temperature Ranges of a Few Degrees C.

A. C^{13}

Atmospheric CO_2

Wood	1.8 $\pm$0.3	Libby and Pandolfi
Marine		
Phytoplankton	0.35	Degens et al.
Plankton	0.5	Eadie
Hot Springs		
Bluegreen Algae	-0.62 $\pm$0.12	Libby and Pandolfi
Los Angeles Water Supply		
Euglena	3.9 $\pm$0.6	Libby and Pandolfi

B. O^{18}

Atmospheric Moisture

Wood	4.4 $\pm$0.3	Libby and Pandolfi
Hot Springs		
Bluegreen Algae	2.2 $\pm$1.0	Libby and Pandolfi

C. D

Atmospheric Moisture

Wood	95 $\pm$19	Libby and Pandolfi
Ground Water		
Peat	3	Schiegl

Table III (Continued)

Measured Isotope Ratios in Algae, Expressed
in Parts per Thousand, Vs. Water Temperature in
Degrees Centigrade

T	δ_{13}*	δ_{18}*
degrees Centigrade	parts per thousand	parts per thousand
30°	+13.7	--
46	- 2.6	-23.3
51	+ 1.4	+17.0
55	- 1.2	+15.1
56	- 3.3	+17.7
64	- 9.3	+22.4

*δ_{13} and δ_{18} are the differences from the values predicted for 50°C by least squares analysis[9].

$$\delta_{13} = \{31.1 - [0.62 \pm 0.12] T\} \text{ ppt}$$

$$\delta_{18} = \{-110 + [2.2 \pm 1.0] T\} \text{ ppt}$$

Temperature Coefficients for Biological Materials Computed** for Cellulose ppt/°C

$a^{18}(O_2)$	0.96
$a^{18}(CO_2)$	1.14
$a^{18}(H_2O)$	0.92
a^{13}	0.36
a(HCOD)	0.4
a(DCOH)	2.0

**See Appendix G.

15

APPENDIX A

MEASUREMENT OF O^{18}/O^{16} RATIO USING A FAST NEUTRON REACTOR

Measurement of ¹⁸O/¹⁶O Ratio Using a Fast Neutron Reactor

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A method has been devised and proven to measure the stable isotope ratio ¹⁸O/¹⁶O for oxygen by neutron activation in a fast neutron reactor. The measurement is made nondestructively on a few grams of water with an accuracy of a few parts in 10,000. At present, measurement to this accuracy requires about 40 min with the reactor running at a power of 250 kw, but by increasing detector sensitivity the method promises to become a routine matter accomplished in less time.

If rapid nondestructive ways of measuring ratios of stable isotopes were available, the use of stable isotopes in research would be greatly aided. We have shown that for the stable isotopes of oxygen the ratio ¹⁸O/¹⁶O can be measured nondestructively in small amounts of water by neutron activation. The activities measured are (a) $^{16}O(n, p)^{16}N$; threshold neutron energy is 10.25 Mev, $\langle \sigma_{16} \rangle (n, p) = 40$ mb, t_{16} (mean life) = 10.3 sec, and $E_\gamma = 6.14$ Mev (68%) and (b) $^{18}O(n, \gamma)^{19}O$; formed by thermal neutron capture, $\sigma_{18}(\gamma, n) = 0.22$ mb, t_{18} (mean life) = 41.8 sec, $E_{\gamma 1} = 1.37$ Mev (60%), and $E_{\gamma 2} = 200$ kev (100%).

It is necessary to irradiate the water in a neutron reactor that has a high fractional flux of fast neutrons (relative to that available in the graphite-moderated reactors) in order for the 10-sec activity to have sufficient intensity. Its gamma ray has a high energy, 6.14 Mev, and so is relatively easy to measure, because the background activities from impurities in water and from the Compton radiation are small at this energy. The 42-sec activity has two gamma rays, namely, 1.37 and 0.2 Mev. That at 1.37 Mev would be the more desirable to measure except that it coincides with a gamma

ray from neutron-activated sodium (which is an abundant impurity) so closely that it cannot be identified separately. Therefore this activity was measured by counting the lower-energy gamma radiation at 200 kev. Here the Compton background is large and is the factor limiting the accuracy of each determination.

The 10- and 42-sec activities are measured at the same time in the same detector, being separated by pulse height analysis, and recorded separately. Water samples in which it is desired to measure the ratio ¹⁸O/¹⁶O are compared with a standard water sample, and the ratio relative to the standard is expressed as a deviation δ^{18} in parts per thousand (‰) according to the definition

$$\delta^{18}(\%_c) = [(R_{meas}/R_{stand}) - 1] \times 1000 \quad (1)$$

The desired accuracy is obtained by irradiating and counting the induced activities of the water sample several times until some hundred million gamma rays have been counted.

EXPERIMENTAL

The Triga Mark I reactor in steady state operation at 250 kw has a thermal neutron flux of $2.8 \cdot 10^{12}$/cm² sec and a fast (fission spec-trum) flux of $3.5 \cdot 10^{12}$/cm² sec at the irradiation position. Water samples of approximately

A-2

5 grams each in plastic vials (purchased from Olympic Plastics Company, Los Angeles, California) containing no intrinsic oxygen were shot into the reactor in the fast pneumatic transfer system and there irradiated for 30 sec, after which they were shot out into a reproducible site in the counting facility. After an interval of 10 sec the induced 10- and 42-sec activities were counted during the next subsequent interval of 30 sec.

Reactor power is maintained at a present level by servo-regulated control rod drives. The insertion of 5 grams of water in plastic vials into the outermost fuel element ring (sample irradiation position) is equivalent to adding a slight amount of reactivity to the core, which is immediately compensated for by automatic control rod adjustment without overshoot. The reactor power is maintained to $\pm 0.13\%$ of the preset level at a confidence level of 95%. The temperature at the sample position ranges from 20° to 25°C during the year but is held constant during any given hour of reactor operation by forced circulation of pool water. The technology and use of the reactor in similar measurements were previously described [Bramblett et al., 1973].

The count in the 200-kev channel was at a rate of 0.2 megacycles, and this is too fast for standard pulse height selection equipment. Therefore a simple pulse height analyzer was built (Figure 1) with integrated circuitry. The system is limited to a maximum count rate of 300 megacycles by the sealers. The sensor was a NaI crystal $\frac{1}{2}$ inch high and 2 inches in diameter glued with a high-viscosity fluorocarbon (Dow Corning 20-057) to a photomultiplier, RCA-6810 A.

The counts observed in 5 grams of normal water (Colorado River water from the public water system of La Jolla, California, for which $^{18}O/^{16}O$ was measured in a mass spectrograph) in a counting interval of 30 sec for the 200-kev radiation (channel 2) and the 6.1-Mev radiation (channel 4) are listed in Table 1. Counting ratios measured at two different power levels of the reactor, namely, at 190 and 250 kev, are strictly comparable, showing that counting losses were negligible. Varying amounts of water enriched in ^{18}O were added to normal water to prepare a series of samples in which ^{18}O was progressively concentrated. The measured ratios of counts in the two channels recording the 200 kev and the 6.0 Mev radiation, respectively, are listed in Table 2 for increasing concentrations and are shown to be linearly dependent on the ^{18}O concentration. As is shown in Table 1, after 24 runs, each of 70 sec, the $^{18}O/^{16}O$ ratio in a given water sample was measured to an overall error of $\pm 0.06\%$ after 24 determinations, each of standard deviation 0.29%. No external perturbations were allowed to influence the reactor during the measurements. The overall standard deviation $(0.29\%/(24)^{1/2} = 0.06\%)$ testifies to the constancy of the ratio of fast neutron flux [Dixon, 1971].
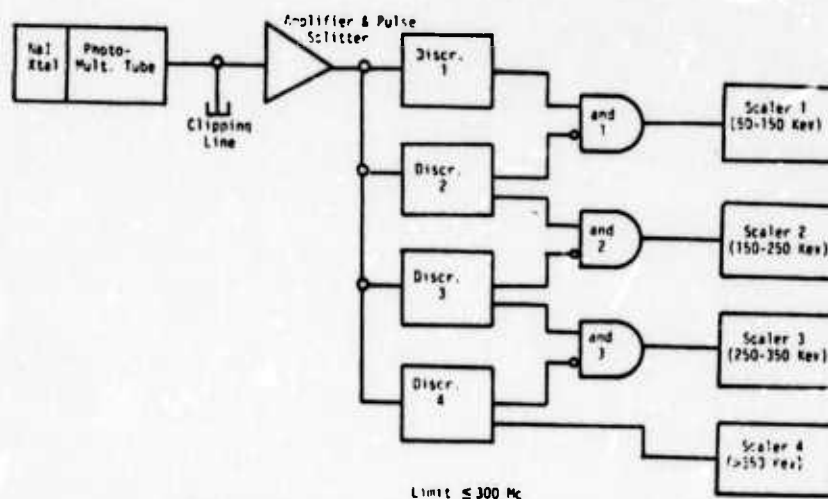

Fig. 1. Block diagram of pulse height selector.

TABLE 1. Observed Decays Proportional to Concentrations of ^{18}O and of ^{16}O and Their Ratios for 24 Experiments on Faucet Water from the Public Water Supply of La Jolla, California

Sample Number	Net Weight, grams	Net Counts		x, Count Ratio Channel 2/Channel 4
		Channel 2	Channel 4	
Sept. 7, 190-kw Reactor Power				
1	4.9640	3,793,063	531,946	7.1305
2	4.9643	3,805,560	536,306	7.0960
3	4.9639	3,872,147	546,752	7.0821
4	4.9681	3,756,711	531,097	7.0735
5	4.9648	3,600,182	507,927	7.0880
6	4.9694	3,734,811	528,492	7.0671
7	4.9661	3,675,843	515,083	7.1364
8	4.9672	3,771,143	531,287	7.0981
9	4.9718	3,708,926	523,682	7.0824
10	4.9666	3,788,234	534,952	7.0814
11	4.9695	3,814,125	538,040	7.0890
12	4.9673	3,758,823	530,097	7.0908
Sept. 12, 250-kw Reactor Power				
1	4.9640	4,123,664	580,767	7.1004
2	4.9643	4,057,737	571,263	7.1031
3	4.9639	4,309,732	608,763	7.0795
4	4.9681	3,975,696	560,343	7.0951
5	4.9648	4,295,982	605,418	7.0959
6	4.9694	4,210,863	597,017	7.0531
7	4.9661	4,230,811	598,442	7.0697
8	4.9672	3,884,063	550,786	7.0518
9	4.9718	3,884,013	549,599	7.0670
10	4.9666	3,874,433	548,264	7.0667
11	4.9695	4,331,802	612,979	7.0668
12	4.9673	4,074,085	574,198	7.0952

30-sec irradiation, 10-sec delay, 30-sec count.
$\langle x \rangle = 7.0858$; $\sigma(\%) = 0.29$; $\sigma_{\langle x \rangle}(\%) = 0.059$.

TABLE 2. Observed Decays Proportional to Concentrations of ^{18}O and of ^{16}O in Water Samples Sequentially Enriched in ^{18}O versus $^{18}O/^{16}O$ Computed from Mass Spectroscopic Measurements

Computed X ^{18}O, wt% of Total Oxygen[*]	Measured Y Channel Ratio, Channel 2/Channel 4	Y Predicted from Regression Line[†]
0.22044	7.0929	7.1050
0.23175	7.1687	7.1692
0.24594	7.1579	7.2497
0.24754	7.2592	7.2587
0.27560	7.4089	7.4190
0.27719	7.4429	7.4270
0.30902	7.6206	7.6974
0.30755	7.5930	7.5991
0.34306	7.7980	7.8005
0.35925	7.8860	7.8924

Pearson product-moment correlation coefficient $r_{XY} = 0.99935$; $\sigma_{prediction} = \pm 0.129\%$ relative; $\sigma_{mean\ prediction} = \pm 0.041\%$ relative.

[*]All but first sample prepared by addition of enriched water. All but first sample measured once. First sample, La Jolle tap water, was measured 24 times (Table 1).
[†]Regression line is obtained from observables: $Y = 5.6721426(X) + 5.854646$. The last number is the ratio of backgrounds in channel 2 to channel 4 in the absence of ^{18}O.

The enriched water was measured by mass spectrograph [*Ritterberg and Pontecorvo*, 1956].

The pneumatic transfer apparatus, Triga Mark I reactor, and timing system have been used as unchanged components in a ^{235}U measurement procedure that delivered 0.37% precision in individual measurements [*Bramblett et al.*, 1973]. Hence the variation in individual channels, $\sigma \approx \pm 2\%$ on September 7 and $\sigma \approx 4\%$ on September 12, is believed to be controlled by the counting equipment. Fortunately, the count ratio proved to be largely independent of the variance of the individual channel. However, it is likely that improvements in counting equipment stability and counting efficiencies will improve both the speed and the precision of the isotope ratio measurement.

CONCLUSION

A nondestructive method of measuring the stable isotope ratio $^{18}O/^{16}O$ in water has been

shown to be possible, rapid, and feasible as a commercial service, to be presently accurate to about 4 parts in 10,000 at a reasonable expenditure of measuring time (about 40 min at present), and to promise future measurements at least to this accuracy in shorter times, when the detector sensitivity has been increased.

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APPENDIX B

MEASURED TEMPERATURE COEFFICIENTS OF
STABLE ISOTOPES IN HOT SPRING ALGAE

MEASURED TEMPERATURE COEFFICIENTS
OF STABLE ISOTOPES IN HOT SPRING ALGAE

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ABSTRACT

The temperature coefficient of three stable isotopes in a blue-green algae, growing in alkaline hot springs at temperatures of 30 °C-68 °C, have been measured. That for oxygen is found to be $+(2.2 \pm 1.0)$ ppt/°C which is larger than the value computed for equilibrium as is to be expected. That for carbon is found to be (-0.62 ± 0.12) ppt/°C; the negative value is attributed to methane formation by copious bacteria so that the system $CH_4 - HCO_3$, which is known to have a negative temperature coefficient, dominates. That for hydrogen is found to be (3.3 ± 0.7) ppt/°C, about twice that computed for equilibrium formation of cellulose. (The quoted errors represent one standard deviation).

RÉSUMÉ

Les coefficients de température de trois isotopes stables pour des algues bleu-vert se développant dans des sources chaudes à des températures de 30 °C à 68 °C ont été mesurés. On a trouvé que le rapport pour l'oxygène est $2,2 \pm 1,0\%$ °C, ce qui est plus élevé que la valeur calculée pour la formation à l'équilibre. Le rapport pour le carbone est $-0,62 \pm 0,12\%$ °C; cette valeur négative est attribuée à la formation de méthane par les nombreuses bactéries, de telle sorte que le système $CH_4 - HCO_3$, dont on sait qu'il a un coefficient de température négatif, domine. Le rapport pour l'hydrogène est $3,3 = 0,7\%$ °C, environ double de celui que l'on peut calculer pour la formation à l'équilibre de la cellulose. (Les erreurs représentent une déviation standard).

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ABSTRACT

The temperature coefficient of three stable isotopes in a blue-green algae, growing in alkaline hot springs at temperatures of $30^{\circ}C$ - $68^{\circ}C$, have been measured. That for oxygen is found to be +(2.2 $\pm$ 1.0) ppt/$^{\circ}C$ which is larger than the value computed for equilibrium formation as is to be expected. That for carbon is found to be (-0.62 $\pm$ 0.12)ppt/$^{\circ}C$; the negative value is attributed to methane formation by copious bacteria so that the system CH_4 - HCO_3^-, which is known to have a negative temperature coefficient, dominates. That for hydrogen is found to be (3.3 $\pm$ 0.7)ppt/$^{\circ}C$, about twice that computed for equilibrium formation of cellulose. (The quoted errors represent one standard deviation.)

INTRODUCTION

Temperature coefficients of some stable isotope ratios in bio-organic material have been measured in marine plankton[1,2], in peat[3], and in wood[4], and are listed in Table I. By measuring these ratios in residual bio-organic material such as sediments, peat beds and tree rings, and combining these data with the measured temperature coefficients it may be possible to evaluate temperatures of past climates, especially if the records of two or more such isotope thermometers are evaluated in each data base. If two or more thermometers record like changes with passage of time the likelihood is enhanced that the changes are truly related to changes in temperature. A second point is that the temperature coefficients which have been measured are only slightly larger than those computed[5] assuming the organic material to have been manufactured at equilibrium (see Table II). In general, the observed effects may be expected to be larger than the equilibrium effect, the latter being the ratio of the rates for the forward and back reactions. In reactions occurring far from equilibrium, only the forward rate applies.

In order for a system to be at equilibrium every chemical or mechanical process must proceed both in the forward and reverse directions a great many times. For example, if a reaction proceeds with evolution of a gas, and if the gas molecules immediately leave the site of formation so that the reverse reaction cannot occur, there can never be equilibrium, nor any reasonable approximation of it. Fractionation of isotopes at equilibrium is caused by the difference between fractionation by the forward rate and fractionation by the reverse rate, the two rates being equal. Distillation of a liquid in a closed container is an example of fractionation at equilibrium. Distillation into a vacuum is kinetic because the reverse reaction is completely inhibited.

The temperature coefficient α, of an isotope ratio R is defined as the derivative of R with respect to a change in temperature T, $\Delta R/\Delta T = \alpha$.

In the present paper we report measurements of the temperature coefficients of O^{18}/O^{16} and D/H in algae growing in hot springs and streams at Rotorua, New Zealand, and find them not much larger than that measured in tree wood[4], (see Table 1).

The ratio C^{13}/C^{12} has also been measured but its temperature coefficient is far smaller than that found in wood[4], probably because the decay of dead algae generates methane which carries off C^{13} leaving depleted bicarbonate to feed the living algae. This temperature coefficient, namely for the system methane-bicarbonate, reduces the overall coefficient to -0.62 ± 0.12 ppt/^{o}C, as will be discussed further in the second section of this paper.

The measurements described here were derived from a limited number of samples very kindly collected by Dr. E. F. Lloyd[6]. We apologize for the small number of the data, but find the results to be important, even if not definitive, because they bear out the fact that temperature coefficients of stable isotopes in organic material are measurable. The field of isotope thermometers in bio-organic material is very new, so that each measurement contributes significantly as is evident in Table I.

The hot springs at Rotorua are a fascinating bio-organic system which will no doubt prove rewarding of further study.

EXPERIMENTAL

Algae, collected at several places in the hot springs at Rotorua[6], New Zealand, of a blue-green variety[7] were freeze dried and analyzed mass spectrometrically for O^{18}/O^{16} and C^{13}/C^{12}. The chemical reactions involved are as follows:

a. For measurement of O^{18}/O^{16}, $HgCl_2$ and algae evolves CO_2 gas[8] when heated; HCl is removed with a quinoline trap.

b. For measurement of C^{13}/C^{12}, the algae were burned to completion in oxygen gas, yielding CO_2.

c. For measurement of D/H, the algae were heated with powdered uranium metal to evolve hydrogen gas.

For each measurement, the amount of reagent used was much larger than needed for stoichiometric proportions with 5 mg of algae, to insure that the reaction was complete so that there would be no fractionation.

The measured ratios are listed in Table III together with the temperature of the water in which the algae were growing when collected. The isotope ratios are expressed in the form,

$$\delta_{13} = \left[\frac{(C^{13}/C^{12})\text{sample}}{(C^{13}/C^{12})_o} - 1 \right] \times 1000$$

$$\delta_{18} = \left[\frac{(O^{18}/O^{16})\text{sample}}{(O^{18}/O^{16})_o} - 1 \right] \times 1000 \qquad (1)$$

$$D = \left[\frac{(D/H)\text{sample}}{(D/H)_o} - 1 \right] \times 1000$$

where $(O^{18}/O^{16})_o$, $(C^{13}/C^{12})_o$ and $(D/H)_o$ have been chosen as the values of the isotope ratios predicted by the least squares analysis[9] for 50^oC. In the

analysis, the ratios are expressed as linear functions of temperature, T, according to

$$\delta = a + bT \qquad \qquad (2)$$

where b is the temperature coefficient.

The values of a and b computed from the measurements are shown in Table III.

Since the water reservoir is much larger than the CO_2 reservoir, it is expected that most of the oxygen in algae will be supplied from the water. It is known for Euglena, a water plant, that this is the case[10]. For exchange of O^{18} in cellulose with O^{18} in water, at equilibrium, the predicted temperature coefficient is +0.92 ppt/^{o}C, compared to which the measured temperature coefficient, +(2.2 ± 1.0) ppt/^{o}C reported in Table I, is positive and larger, as is to be expected for a natural process which is likely to involve dynamic effects. Since oxygen gas is evolved in photosynthesis, according to the schematic reaction,

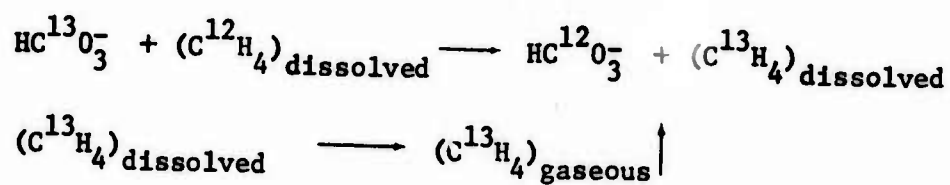$$CO_2 + H_2O \longrightarrow cellulose + O_2 \uparrow$$
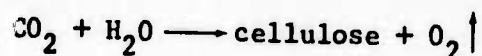
and leaves the site of the reaction, the reverse reaction is inhibited, and equilibrium considerations would not be applicable.

The temperature coefficient of C^{13}/C^{12} evaluated from the measurements is _negative_. This may be accounted for as follows. The water issuing from the hot springs is strongly alkaline (pH ~8.4) and in addition contains masses of decaying algae and bacteria[7] in large amounts, so that methane is being evolved by decay according to the schema,

$$HCO_3^- + bacteria + dead\ cellulose \longrightarrow CH_4 \uparrow + decaying\ organic\ matter$$
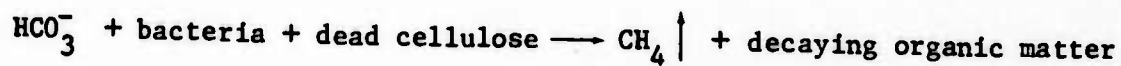
Namely the system is dominated by exchange of C^{13} in the abundant inorganic system

$$HC^{13}O_3^- + (C^{12}H_4)_{dissolved} \longrightarrow HC^{12}O_3^- + (C^{13}H_4)_{dissolved}$$

$$(C^{13}H_4)_{dissolved} \longrightarrow (C^{13}H_4)_{gaseous}\uparrow$$

so that the liquid system is depleted of C^{13}.

The equilibrium fractionation factors for the system $CO_2 - HCO_3^- - CH_4$, calculated by Bottinga[11], show that C^{13} is enriched in CH_4 with respect to HCO_3^-, increasingly at high temperatures, and that the minimum value of the temperature coefficient (predicted for equilibrium) is negative, namely -0.32 ppt/$^{\circ}$C. The actual temperature coefficient is expected therefore to be negative and somewhat larger. (Since methane is evolving, dynamic effects clearly are playing a role.) Thus methane evoluation by bacterial decomposition of the dead algae carries off C^{13}, leaving the aqueous HCO_3^- depleted in C^{13} so the growing algae have less C^{13} at high temperatures. Farther down stream where the water is cooler, this process of enrichment, being temperature dependent, has a smaller fractionation factor. Thus in this case the temperature dependence of C^{13}/C^{12} in algae acts as a poor thermometer, one appropriate only to the particular hot springs of Rotorua, New Zealand.

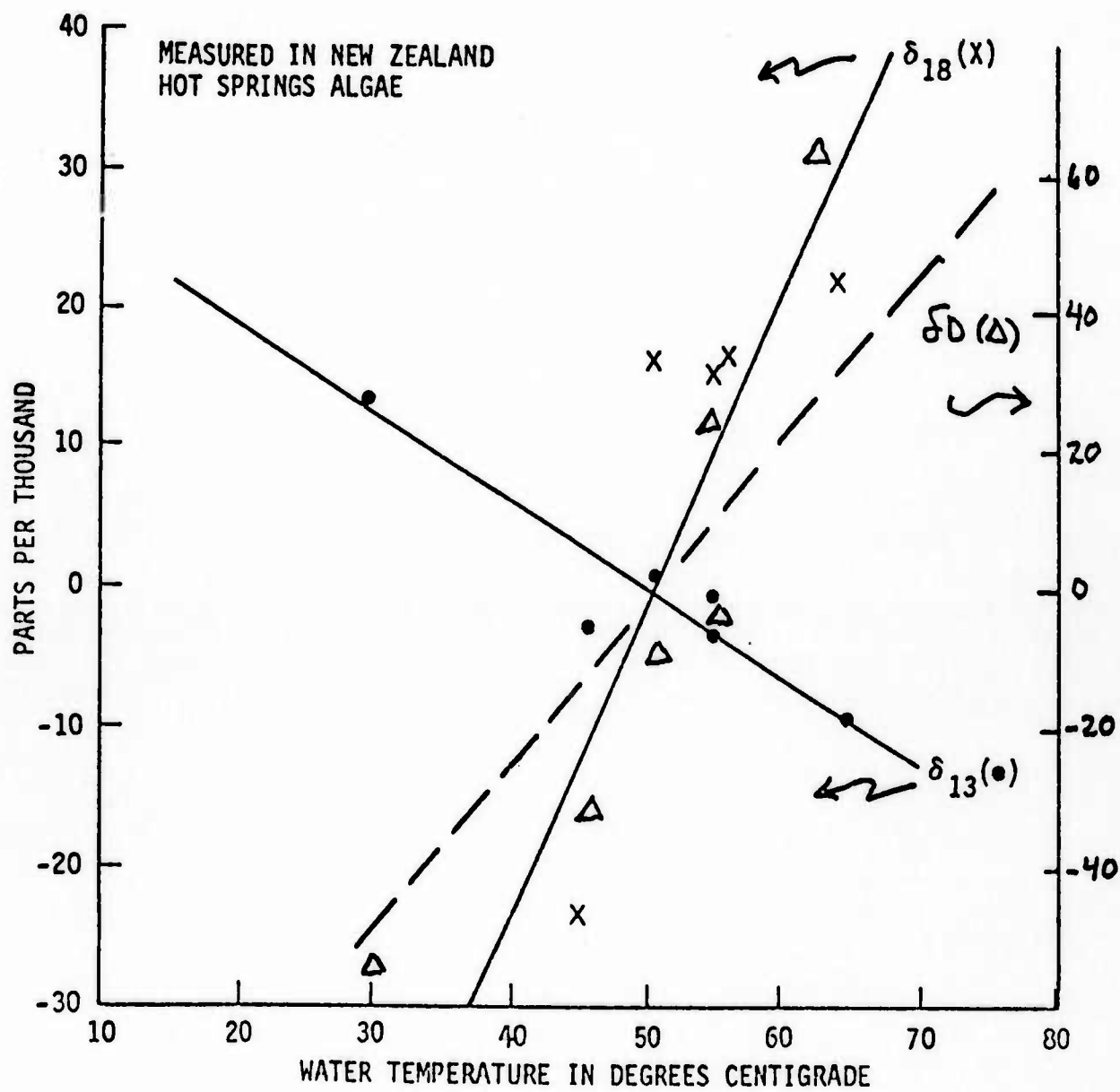Figure 1: δ^{13}, δ_D and δ^{18} (relative to deltas at 50°C) vs. water temperature.

TABLE 1:   Experimental values of temperature coefficients of isotope
            ratios in bio-organic material.

A. C^{13}

           Atmospheric CO_2

Wood	1.8 ± 0.3	Libby and Pandolfi

           Marine

Phytoplankton	0.35	Degens et al
Plankton	0.25	Sackett et al
Plankton	0.5	Eadie

           Hot Springs

Bluegreen Algae	-.62 ± .12	Libby and Pandolfi

B. O^{18}

           Atmospheric Moisture

Wood	4.4 ± 0.3	Libby and Pandolfi

           Hot Springs

Bluegreen Algae	2.2 ± 1.0	Libby and Pandolfi

C. D

           Atmospheric Moisture

Wood	95 ± 19	Libby and Pandolfi

           Ground Water*

Peat	3	Schiegl

           Hot Springs

Blue Green Algae	3.3 ± 0.7	Libby and Pandolfi

*See Reference 12 for discussion of ground water.

TABLE II: Temperature coefficients of isotope ratios in bio-organic material computed for manufacture at equilibrium.

COMPUTED* FOR CELLULOSE ppt /°C

$a^{18}(O_2)$ 0.96

$a^{18}(CO_2)$ 1.14

$a^{18}(H_2\dot{O})$ 0.92

a^{13} 0.36

$a(HCOD)$ 0.4

$a(DCOH)$ 2.0

*FROM REFERENCE 5.

TABLE III: Delta values for isotope ratios in blue green algae growing in hot springs, Rotorua, New Zealand, and temperature coefficients evaluated from the measurements.

T degrees Centigrade	δ_{13}* parts per thousand	δ_{18}* parts per thousand	D parts per thousand
30°	+13.7	---	-56
46	-2.6	-23.3	-29
51	+1.4	+17.0	-13
55	-1.2	+15.1	-9
56	-3.3	+17.7	+22
64	-9.3	+22.4	+64

* The deltas are the differences from the values predicted for 50°C by least squares analysis[9].

$$\delta_{13} = \left\{ 31.1 - [0.62 \pm 0.12] \; T \right\} \quad \text{ppt}$$

$$\delta_{18} = \left\{ -110 + [2.2 \pm 1.0] \; T \right\} \quad \text{ppt}$$

$$\delta_D = \left\{ -165 + (3.30 \pm 0.73)T \right\} \quad \text{ppt}$$

The relatively large errors in the evaluated temperature coefficients probably relate for the most part to fluctuations in water temperature issuing from the hot springs as described in Reference 7.

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3. W. E. Scheigl, "Deuterium Content of Peat as a Paleo-Climate Recorder", Science 175, 512-513 (1972).

4. L. M. Libby and L. J. Pandolfi, "Calibration of Two Isotope Thermometers, C^{13}/C^{12} and O^{18}/O^{16}, in a European Oak Using Official Weather Records", presented at the International Meeting on Climate Parameters, May 17-22, University of East Anglia, Norwich, Norfolk, England.

5. L. M. Libby, "Multiple Thermometry in Paleoclimate and Historic Climate", J. Geophysical Research, 77, 4310 - 4317 (1972), Temperature coefficients for cellulose have been computed for equilibrium; those for other organic materials will be closely equal because bond strengths are about equal for C-H, C-O, OH, etc., bonds in all such materials; for example, the stretching frequency of C-H is always around 2960 cm^{-1}, of O-H always around 3680 cm^{-1}, etc.

6. We are indebted to Dr. E. F. Lloyd, Department of Scientific and Industrial Research, New Zealand Geological Survey, Rotorua, New Zealand for collecting the algae and measuring the temperatures of the water where they were growing.

7. T. D. Brock and M. L. Brock, "Microbiolcgical Studies of Thermal Habitates of the Central Volcanic Region, North Island, New Zealand", New Zealand Journal of Marine and Fresh Water Research, 5, pg. 233-258 (1971), identify the algae as Mastigocladus luminosus, state that the water temperatures at the spring outlets can vary upward by as much as 5° during periods of much rain, killing large masses of algae at the hottest temperatures ($68^{o}C$) and causing growth of large masses of bacteria. They report the spring water to be strongly alkaline (pH 8.25 - 8.45).

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12. M. McComas, J. Kempton, and K. Hinkley, "Geology, Soils, and Hydrology of Volo. Bog and Vicinity, Lake County, Illinois", Illinois State Geological Survey, Nov. 1972, No. 57, Urbana Illinois (see page 19) defines ground water as water moving laterally below the water table, subsequently discharged to the surface, providing the water for permanent swamps and bogs. This water does not necessarily have the isotopic composition of rain.

APPENDIX C

ISOTOPE THERMOMETERS IN OAK TREE RINGS
CALIBRATED USING OFFICIAL WEATHER RECORDS

CALIBRATION OF ISOTOPE THERMOMETERS
IN AN OAK TREE USING OFFICIAL WEATHER RECORDS

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ABSTRACT

The stable isotope ratios of carbon, oxygen and hydrogen have been measured for an oak from central Germany in wood samples consisting of roughly 3 years each, for the years 1712-1954 A.D. and correlated with the existing weather records for these years, from England, nearby Basel, and Geneva. In this way, the temperature coefficients for O^{18}/O^{16} are evaluated as (5.29 ± 0.68), (2.91 ± 0.41) and (2.86 ± 0.52) respectively, the coefficients for C^{13}/C^{12} are evaluated as (2.73 ± 0.67), (2.01 ± 0.37) and (2.37 ± 0.41), respectively, and for D/H, as (89 ± 16), (67 ± 6) and (71 ± 8) in units of parts per thousand per degree Centigrade (ppt/°C). Use of these three numerically calibrated isotope thermometers may allow the study of air temperature changes in climate before 1712.

RÉSUMÉ

Les rapports des isotopes stables du carbone de l'oxygène et de l'hydrogène ont été mesurés dans un chêne d'Allemagne centrale. Chaque échantillon de bois représentait environ 3 ans de 1712 à 1954 A.D. Ces résultats ont été corrélés avec les enregistrements météorologiques existant pour ces années en Angleterre, près de Bâle et à Genève. De cette façon, on peut évaluer des coefficients de température pour $^{18}O/^{16}O$ qui sont respectivement 5,29 ± 0,68; 2,91 ± 0,41 et 2,86 ± 0,52, les coefficients pour $^{13}C/^{12}C$ sont respectivement 2,73 ± 0,67; 2,01 ± 0,37 et 2,37 ± 0,41 et pour D/H 89 ± 16; 67 ± 6 et 71 ± 8 en pour mille par °C. L'utilisation de ces thermomètres isotopiques numériquement étalonnés peut permettre l'étude des variations de la température de l'air avant 1712.

Title   ISOTOPE THERMOMETERS IN OAK TREE RINGS CALIBRATED USING OFFICIAL WEATHER RECORDS

The *Proceedings of the National Academy of Sciences, U.S.A.* publishes brief reports of original research. It is not a specialized but an interdisciplinary journal. Sometimes, preliminary findings of major importance are published in the Proceedings without full documentation.

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Comments (use additional pages if necessary; send original and two copies).

ISOTOPE THERMOMETERS IN OAK TREE RINGS CALIBRATED
USING OFFICIAL WEATHER RECORDS

Annual tree rings are a most valuable source of information, perhaps the only year-to-year source of information on environmental and climatic changes during the past. There are now tree-ring sequences available that go back more than 7,000 years, and the study of this material is most desirable. Every effort to use it is most commendable. This paper reports the discovery of an impressive correlation between stable isotope ratios in the wood of an oak and temperature records in Europe for the 18th and 19th centuries. Should this correlation turn out to be a general phenomenon observable in any kind of wood, then it would provide the best possible way for determining climatic variations for the time prior to that when meteorological records started. I strongly recommend that this paper be published, as it undoubtedly will stimulate further research in this important field, which is of interest in a large number of fields of science. I consider the length of the paper and the way the findings are presented to be adequate.

Please return to:

 Hans S. . . . . .

(Signature and typed name of referee on above copy only)

Hans . . . . .
Professor of . . . Geochemistry

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CALIBRATED USING OFFICIAL WEATHER RECORDS

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ABSTRACT

The stable isotope ratios of carbon, oxygen and hydrogen have been measured for an oak from central Germany in wood samples consisting of roughly three years each, for the years 1712 - 1954 A.D. and correlated with the existing weather records for these years, from England, nearby Basel, and Geneva. In this way, the empirical temperature correlations can be expressed by the following coefficients for O^{18}/O^{16}: (5.29 ± 0.68), (2.91 ± 0.41) and (2.86 ± 0.52) respectively, the corresponding coefficients for C^{13}/C^{12} are (2.73 ± 0.67), (2.01 ± 0.37) and (2.37 ± 0.41), respectively, and for D/H (89 ± 16), (67 ± 6), and (71 ± 8) in units of parts per thousand per degree Centigrade (ppt/°C). Use of these three numerically calibrated isotope thermometers may allow the study of air temperature changes in climate before 1712.

INTRODUCTION

Information on climate is stored in natural data banks, namely in bio-organic materials that are deposited year after year and thereafter remain undisturbed. In particular, tree rings in living and dead trees may provide a worldwide record of climate for the last few thousand years. The information is in chemical form, namely in the ratios of stable isotopes; that is, variations in air temperature, and therefore in the temperature at which the wood is formed, cause variations in the stable isotope ratios in the new wood as it grows. An additional variable is the temperature of formation of water which nourishes the tree.

The justification for regarding stable isotope ratios in land plants as thermometers for air temperature is twofold. Although we also need to know the isotope ratios in atmospheric CO_2 and of rainwater which nourishes the plants, there is good reason to believe that in the long term average, atmospheric CO_2 has remained unchanged for a long time, say millions of years, so this is not an unknown. The isotope ratios in precipitation have been studied all over the world's surface for the last 15 years and have been reported in the data compilations of the International Atomic Energy Agency. So we know the percent of O^{18}/O^{16} and D/H in rainwater as a function of altitude and latitude and longitude of the surface of the earth. These ratios may have undergone variations in the past caused by changes in the global temperature.[1]

Consequently, stable isotope ratios in land plants depend on several temperature dependent functions. The resulting temperature dependence has been observed experimentally.

When a plant dies, the record of the air temperature may be stored in its tissues, in the form of the numerical values of the stable isotope ratios.

The most important of these ratios are D/H, C^{13}/C^{12}, O^{18}/O^{16}, N^{15}/N^{14}, and S^{34}/S^{32}.

The ratios were measured for three independent elements in the wood, H, C, O, that is, the records from three thermometers were read, so that it appears that temperature variations in the past can be evaluated, with some confidence and the observed variations seem truly to be correlated with temperature changes.

Factors that can be calculated quantitatively are the equilibrium temperature coefficients of the stable isotopes of H, C, and O in cellulose (trees being 69% cellulose, the remainder being mainly lignin). They are large enough so that variations of a few degrees in air temperature should cause measurable effects.[2] The values of the coefficients for D/H, C^{13}/C^{12}, and O^{18}/O^{16} have been computed in Reference 2 (see Table 1) on the assumption that cellulose is formed at chemical equilibrium. It is known that at least for C^{13}/C^{12} in marine plankton[3,4], and for D/H in peat,[5] the measured coefficients are approximately equal to the computed values. In general, however, the observed effects may be expected to be larger than the equilibrium effect, the latter depending on the difference of the rates for the forward and back reactions. Two temperature effects are probably involved, the first characterizing manufacture of cellulose and the second characterizing manufacture of rain water. Eventually these effects should be separated. Until now, the temperature coefficients in trees had not yet been measured.

Anyhow, because of variations in O^{18}/O^{16} and D/H rati in precipitation, the stable isotope thermometers in trees must be calibrated; namely, their observed variations in rings formed in the last few hundred years must be compared with the official weather records of variations in air temperature in the neighborhood of the tree, to yield numerical values for the changes in isotope ratios per degree Centigrade change in temperature.

Calibration of the effects of climate on stable isotope ratios in living trees must be undertaken judiciously, keeping in mind that numerical air temperatures have been recorded at best for no more than about three hundred years in Europe, and for only about one hundred years in America. Furthermore, both the temperature records and the recently formed tree rings may be perturbed by local climate changes caused by increasing heat and air pollution produced by the cities growing up around the existing weather stations and around the trees. Also the introduction of fossil fuel CO_2 (Suess Effect) is expected to perturb the C^{13}/C^{12} ratios in rings grown after 1890.

In the present paper are reported measurements of C^{13}/C^{12}, O^{18}/O^{16}, and D/H in the rings of an oak[6] which grew in Aalen, Germany, $10^{o}11'$ east, $48^{o}50'$ north, about half way between Mannheim and Münich, from 1700 to 1965 A.D. Air temperature records exist for nearby Basel[7] since 1755, for Geneva[7] since 1768, and for England[8] from 1698. The measured isotope ratios as a function of tree ring data have been compared with these official temperature records for 1712 - 1954 A.D. using the dated tree ring sequence[6] to determine the corresponding age of the tree rings in years. In this way, temperature coefficients of the stable isotope ratios have been evaluated, as a phenomenological effect, without attempting to separate the effect of manufacture of cellulose from that for manufacture of precipitation.

THEORETICAL

Of the various factors that determine the isotope ratio for a given element in plant material, at least one, the thermodynamic isotope exchange constant, can be calculated rigorously. Consider, for example, exchange of CO_2 and cellulose at equilibrium according to the schematic reaction:

Consider, for example, exchange of CO_2 and cellulose at equilibrium according to the schematic reaction:

$$C^{13}O_2 + (H-C^{12} - OH)_n \longrightarrow C^{12}O_2 + (HC^{13} - OH)_n$$
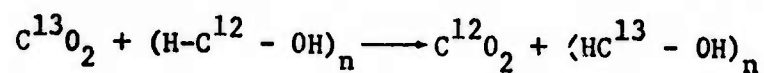
The equilibrium constant K is given by,

$$K = \frac{Q(C^{12}O_2)}{Q(C^{13}O_2)} \quad \frac{Q(HC^{13}OH)}{Q(HC^{12}OH)}$$

where the Q's depend only on temperature according to

$$Q = \frac{e^{-(1/2)h\omega/kT}}{[1 - e^{-h\omega/kT}]}$$

for each frequency.

These ω's are frequencies of vibration, and depend on the force constant k and the reduced mass, m, of each two vibrating atoms, according to:

$$\omega = 2\pi\sqrt{\frac{k}{m}}$$

For a given pair of atoms bound to each other, the force constant, or spring constant k, has the same value regardless of isotopic mass. The isotopic effect occurs because m is different for different masses, so the ω's are different.

C-9

For the C-O bond for example, there are four different frequencies corresponding to the isotopic pairs,

$$C^{12}O^{16}, \ C^{13}O^{16}, \ C^{12}O^{18}, \ C^{13}O^{18}$$
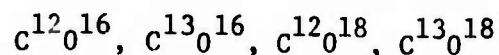
Thus, in land plants the equilibrium constant K depends on air temperature, T. The equilibrium constants $K(300^{\circ}C)$ and $K(273^{\circ}C)$ for the formation of cellulose at equilibrium have been computed according to the schematic reaction:

$$CO_2 + H_2O \longrightarrow (H - C - OH)_n + O_2$$
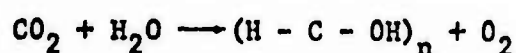
The temperature coefficient α for exchanges of the stable isotopes between cellulose and CO_2, or H_2O, or O_2 is then obtained from the computed K's according to:

$$\alpha = \frac{K(300^{\circ}C) - K(273^{\circ}C)}{27^{\circ}C}$$

These computed coefficients[2] for exchange at equilibrium are found to be large enough to measure, see Table 1. If exchange occurs away from equilibrium, (these are called kinetic effects), the temperature coefficients can be larger. An example of a kinetic effect is evolution of a gas, e.g., O_2 in the above example, preventing the reverse reaction from occurring and hence preventing equilibrium conditions to be reached.

In an equilibrium process, atoms and molecules must react and back-react many times. If a substance leaves the site of the reaction as soon as it is formed, there can never be equilibrium. For instance, if water vapor escapes into a vacuum at the instant it leaves the surface of liquid water, or if oxygen leaves a tree leaf as soon as formed in photosynthesis, these are dynamic effects and preclude equilibrium.

Of the five principle isotope thermometers in bio-organic material, no two atoms, H, C, O, N and S are tied through the same set of bonds. For example, in cellulose H is tied to C and to O; O is tied to H and C; and C is tied to O and H and other carbons. Thus there are three independent thermometers, and two more if N and S are added. In shell there is only one thermometer because C and O are tied through the same bond. If one isotope ratio changes, there is uncertainty as to the cause. But if three isotope ratios depend on temperature as well as on other parameters, and all three change simultaneously, then it is likely that the changes were caused by temperature change.

EXPERIMENTAL

In a 2" thick slice cut across the tree, a groove 1/3" wide and 1/3" deep was milled perpendicular to the tree rings, that is along a radius of the tree, from the innermost (oldest) part of the tree out to the bark (see Figure 1). Each time that the milling tool had moved 1/3", the sawdust produced was collected into an individual vial with the aid of a camel's hair brush. Each sample consisted of sawdust from about 3 or 4 rings, depending on the variations in ring widths, the total number of samples being 68 for the time span 1712 - 1954 A.D.

The stable isotope ratios were measured in the sawdust samples by mass spectrometry. The spectrometer has a very small quartz manifold, of volume about 100 cm^3. About 5 mg of sawdust were used for each measurement. The chemical reactions used were as follows:

a. For measurement of C^{13}/C^{12}, the sawdust was burned to completion in oxygen gas, yielding CO_2.

b. For measurement of O^{18}/O^{16}, $HgCl_2$ + sawdust evolves CO_2 gas[9] when heated; HCl is removed with a quinoline trap.

c. For measurement of D/H, sawdust is heated with powdered uranium, to evolve H_2.

For each measurement, the amount of reagent used was much larger than needed for 5 mg of sawdust, to insure that the reaction was complete so that there would be no fractionation. The residue was inspected, after cooling, for the same reason. The measured ratios are listed in Table I along with the tree ring dates as determined by the Münich Forest Botanical Institute[6]. The measured variations in stable isotope ratios in tree rings are seen to be large, of the order of a few parts per thousand (ppt), expressed in the form:

$$\delta_{13} = \left\{ \frac{(C^{13}/C^{12})_{sample}}{(C^{13}/C^{12})_0} - 1 \right\} \times 1000$$

$$\delta_{18} = \left\{ \frac{(O^{18}/O^{16})_{sample}}{(O^{18}/O^{16})_0} - 1 \right\} \times 1000$$

$$\delta_{D} = \left\{ \frac{(D/H)_{sample}}{(D/H)_0} - 1 \right\} \times 1000$$

The normalizing ratios $(C^{13}/C^{12})_0$, $(O^{18}/O^{16})_0$ and $(D/H)_0$ may be defined in any convenient way, and here have been chosen arbitrarily as the measured ratios for the years 1712 - 1714 A.D. for computing the delta values listed in Table I.

The sapwood of the oak extended over about 30 tree rings. That is, sapwood changed into inert hardwood some 30 years after it was manufactured, and thus for about 30 years each tree ring was bathed in flowing sap from ground water. Consequently, it is to be expected that oxygen in the alcohol groups of cellulose, its modular formula being $(HCOH)_n$, is exchanging with sap water, and thus that the stable isotope ratio of oxygen in each ring is averaged over about 30 years[10]. There is less reason to believe that carbon in the wood is exchanging with carbon dioxide dissolved in sap, but it has not been proven that there is no exchange[11,12]. On this account, the measured isotope ratios are reported in the form of a running average over 9 samples at a time, namely as an average over the time that a given ring is sapwood. Winter air termparatures, from official weather records[7,8] averaged in the same way, are also listed in Table 1. Temperatures for January, February and March show the major increase since the Little Ice Age (1440-1850 A.D.), whereas the summer temperatures then were not much different from now[13]. So the average yearly temperatures vary in the same way as the average temperatures of January, February and March, but with a somewhat smaller amplitude. Oak trees make

the greatest growth of the year in early spring when the ground thaws and the winter's accumulation of precipitation melts, so it seems reasonable that they will be sensitive to late winter temperatures, especially for isotopes of oxygen and hydrogen which come from the melt water and depend on the temperature at which precipitation formed.

The carbon ratios (δ_{13}) for the years 1890 - 1950 A.D. have been corrected for fossil carbon production, the maximum correction, that for the year 1950 A.D., taken as +8.4% or a maximum increase of +2.1 ppt in δ_{13}. This correction was estimated as follows. In wood from rings of 1920 A.D. two radiocarbon dates were measured[14] as 375 ± 35 years old with respect to 1950 A.D., whereas the actual age is 1950 - 1920 = 30 years, corresponding to 4.2% dilution of atmospheric $C^{14}O_2$ by inert CO_2 produced by man's burning of coal and oil up to 1920. In 1950 the correction for C^{14} at this particular place should be 8.4% and the correction for C^{13} dilution in atmospheric CO_2 therefore should be 8.4% of 25 ppt[14] or 2.1 ppt; see further discussion in Reference 15.

The ratios and temperatures were correlated by least squares analysis, expressing the ratios in the form,

$$\delta = a + bT \qquad\qquad [2]$$

and evaluating the coefficients a and b, (a is the value of δ at T = 0, and b is the temperature coefficient). Their numerical values are shown in Table II and plotted in Figures 2 and 3. The average of the temperature coefficients for O^{18}/O^{16} computed from air temperatures at Basel and Geneva, (these places being closer to the tree than is England) is (2.88 ± 0.36)ppt/^{o}C. This may be compared to the value of 2.2 ± 1.0 ppt/^{o}C measured for blue-green algae[16]. The average for C^{13}/C^{12} in oak is 2.19 ± 0.25 ppt/^{o}C, which is a good deal larger than the value of 0.35 ppt/^{o}C measured by Eadie[4] for marine phytoplankton.

The oak tree oxygen depends on changing rain water however, whereas the O and H in the water plants should be from an unchanging water supply. The average for D/H is 69 $\pm$ 4, and it also is large compared with the value of 3 ppt/^{o}C derived from Schiegl's measurement. A comparison is made of the averages of coefficients for England, Basel, and Geneva temperatures with theoretical coefficients in Table III. In a manner of speaking, trees store old rainwater. So, to the isotope fractionation caused by evaporation of water vapor from the oceans and precipitation as rain, the tree adds a further fractionation caused by absorption of ground water into the salt and sugar solutions in the root system, and by manufacture into bio-organic material. The combination of these processes appears to produce large temperature coefficients.

If the correlations reported for this oak are general for all oaks, then this effort can be very useful.

YEARLY FLUCTUATIONS, SIGNAL "NOISE"

Yearly variations of C^{13}/C^{12} in atmospheric CO_2 resemble a sine function with a few parts per thousand peak to peak amplitude; the amplitude may be geographically dependent[17]. All available data on this seasonal variation appear to show depletion of C^{13} in the winter, enhancement in summer, and the greatest rate of change in spring and fall. Thus, if spring comes early or late, namely if the tree begins it major growth of a new ring early or late with respect to the inflection point of the sine curve, the C^{13}/C^{12} ratio in the new wood may be depleted or enhanced by up to 3 ppt, with respect to the average ratio.

One expects that similar yearly variations occur for O^{18}/O^{16} in atmospheric CO_2. For comparison it is known that there is a similar seasonal variation[18] both for CO_2^{18}/CO_2^{16} and for $C^{13}O_2/C^{12}O_2$ in the atmosphere of a few parts per thousand. However, this source of year to year variations in the oxygen isotope ratio in wood is probably less than the variations in rain and snow.

Namely, at any given geographical place, the O^{18}/O^{16} ratio in rain water varies by some 10 ppt during the year[19], even fluctuating by several parts per thousand month by month and day by day, depending on the temperatures at which sea water evaporated and at which the precipitation formed, and therefore on the altitude of the clouds (see Figure 4). This dependence on temperature is exact but the dependence on air temperature at ground level is valid only on the average (see Figure 5), indicating that the average air temperatures aloft where precipitation forms are correlated to average air temperatures at ground level. At higher latitudes where trees make a rapid spring growth consuming the melt water from accumulated winter snow, both that on the surface of the ground and that stored in the soil as winter frost,

the new tree ring binds oxygen whose isotope ratio represents an average over the winter time precipitation.

If the winter has been colder than average, the melt water is depleted in O^{18}, and if warmer than average, then it is enriched, to the degree of several parts per thousand (see Figure 4 and 5). Study of the IAEA data shows that δ_{18} is independent of total rainfall.

It is because of the large yearly fluctuations in the air temperature data that we have plotted their running averages and used them in the least squares fits.

Comparison of a plot of δ_{18} vs δ_D in tree rings (see Figure 6) with that in precipitation shows that the slope of 8 for precipitation no longer obtains, probably because the rates of exchange of D and O^{18} between cellulose and sap are quite different from each other. (Thus, it may be now possible to study dynamic physiology of trees, as a research independent of the study of climate.)

In the long term of tens of hundreds of years, a distinct climate change may record itself by a distinct change in the O^{18}/O^{16} ratio in precipitation and therefore in the tree wood manufactured after the climate change compared with that from before. It is known that in a water plant, Euglena, 90% of the bound oxygen is suppl   from water[20]. In trees, the source of oxygen is not known, but because the amount of water in the tree is so much greater than the amount of dissolved carbon dioxide, it is to be expected that the major source is rainwater, even if CO_2 and H_2O are in equilibrium.

CONCLUSION

Every kind of thermometer has to be calibrated. The stable isotope ratios in tree wood depend partly directly, partly indirectly on the temperature at which the wood was manufactured. The present paper reports the phenomenological calibration of the oxygen, carbon and hydrogen isotope ratios in a European oak. The long term increase in air temperatures from the Little Ice Age to the present offered the opportunity to make this calibration. In each case the measured temperature coefficients are larger than those computed assuming the wood to have been manufactured in equilibrium with CO_2 and H_2O, as is to be expected because kinetic effects, no doubt, play a role, and because in formation of precipitation used in the manufacture of cellulose the temperature coefficients of O^{18} and D are large and positive. In this first attempt to study isotope thermometers in tree rings we have lumped the temperature coefficients for cellulose manufacture with the temperature coefficients for precipitate formation for an evaluation of the over-all phenomenological coefficient. We realize that many problems must be solved for a better understanding of these effects, that woody material must be grown under controlled conditions for evaluation of the cellulose manufacture coefficients, that other oaks must be compared with this oak, and that oaks should be compared with other kinds of trees. Using the measured temperature coefficients of these thermometers, and using measured isotope ratios in chronologic sequences of tree rings manufactured before 1712, it now may be possible to evaluate the European climate from the centuries before the advent of mechanical thermometers[22]. Use of more than one thermometer increases the likelihood that temperature effects are being observed. Other isotope thermometers in tree rings, namely nitrogen and sulfur, should also have measureable temperature coefficients.

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Therefore, it is reasonable to take the C^{13}/C^{12} ratio in the unperturbed
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to the correction of an increase in δ_{13} by 2.1 ppt in 1950 used in the
present paper.

Also relevant to this matter are measurements by W. Kane and H. Suess
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on Manhattan Island, grown between 1930 and 1950, before atmospheric bomb
testing in 1970, and measurements by L. Pandolfi (private communication) of
depletions in C^{14} by 5 ppt in greasewood as far east of Los Angeles as Las
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    are now. Between 1700 and 1950 A.D. one does not expect that there was
    a change in average world wide ocean surface temperature of importance to the
    effects reported in the present paper, and instead that the effects presented
    here relate to dynamic biological processes and to temperature dependence of
    isotope fractionation in precipitation.

TABLE I - Measured isotope ratios in dated oak tree rings and

corresponding winter temperatures from official weather

records for England, Basel and Geneva.

SAMPLE NUMBER	δ_{13} ppt	δ_D ppt	δ_{18} ppt	T_{Eng} °C	T_{Basel} °C	T_{Geneva} °C	DATE SPAN
1	0	0	0	4.26			1712 - 1714
2	1.13	156.0	3.62	3.89			1715 - 1717
3	1.90	181.0	6.35	3.98			1718 - 1720
4	3.41	141.0	6.35	4.24			1721 - 1723
5	3.56	110.0	7.20	4.36			1724 - 1726
6	3.87	131.0	7.96	4.30			1727 - 1731
7	4.32	103.0	8.36	4.39			1732 - 1734
8	4.02	73.2	8.28	4.46			1735 - 1737
9	4.09	51.1	7.88	4.38			1738 - 1743
10	4.55	23.2	7.12	4.52			1744 - 1747
11	4.47	46.4	6.67	4.52			1748 - 1750
12	3.49	31.7	7.24	4.25			1751 - 1753
13	3.71	58.0	5.39	4.00	0.06	(0.14)	1754 - 1758
14	3.11	63.5	5.59	4.03	0.98	(2.30)	1759 - 1761
15	3.03	45.7	5.11	3.98	0.81	(1.90)	1762 - 1764
16	3.41	54.2	4.38	3.95	0.98	(2.30)	1765 - 1767
17	4.32	60.3	4.18	3.97	1.00	2.34	1768 - 1772
18	4.02	55.7	3.29	3.86	0.95	2.72	1773 - 1775
19	4.40	62.7	4.50	3.73	1.02	2.49	1776 - 1777
20	3.64	68.9	3.21	3.70	1.21	2.25	1778 - 1779
21	4.24	75.1	2.09	3.69	1.29	2.30	1780 - 1783
22	4.85	48.0	2.01	3.84	1.35	2.31	1784 - 1786
23	5.46	41.8	1.93	3.77	1.12	2.17	1787 - 1791
24	5.46	37.9	1.85	3.82	1.20	2.00	1792 - 1794
25	3.49	39.5	3.78	3.82	1.33	2.07	1795 - 1796
26	3.00	29.4	3.94	3.66	1.18	1.85	1797 - 1801
27	2.73	51.1	4.22	3.86	1.46	2.09	1802 - 1804
28	2.12	45.7	3.78	3.89	1.45	2.11	1805 - 1808
29	1.21	15.5	3.22	3.93	1.23	1.90	1809 - 1811
30	1.36	10.1	4.46	3.99	1.23	1.98	1812 - 1814

TABLE I (continued)

SAMPLE NUMBER	δ_{13} ppt	δ_0 ppt	δ_{18} ppt	T_{Eng} ^oC	T_{Basel} ^oC	T_{Geneva} ^oC	DATE SPAN
31	0.60	12.4	4.98	3.93	1.14	1.91	1815 - 1818
32	0.83	9.3	4.50	4.01	1.34	2.06	1819 - 1822
33	0.45	18.6	4.86	3.98	1.31	2.06	1823 - 1826
34	2.80	37.2	3.50	3.95	1.20	1.98	1827 - 1829
35	2.88	42.6	4.06	4.14	1.36	2.16	1830 - 1833
36	3.87	20.9	3.69	4.04	1.21	2.07	1834 - 1837
37	3.33	31.7	2.45	4.01	1.10	1.94	1838 - 1843
38	4.32	33.3	3.62	4.04	1.24	2.06	1844 - 1848
39	4.40	47.2	2.81	4.06	1.37	2.11	1849 - 1852
40	3.34	65.8	3.58	4.14	1.52	2.21	1853 - 1856
41	5.23	72.0	4.50	4.09	1.53	2.20	1857 - 1861
42	5.84	71.2	3.66	4.15	1.73	2.42	1862 - 1866
43	5.76	57.3	4.14	4.16	1.70	2.39	1867 - 1872
44	5.91	61.9	2.93	4.15	1.56	2.36	1873 - 1876
45	5.15	78.9	3.54	4.28	1.63	2.38	1877 - 1880
46	4.47	80.5	4.54	4.34	1.73	2.49	1881 - 1884
47	5.23	89.0	5.59	4.37	1.71	2.49	1885 - 1888
48	5.53	87.5	5.59	4.36	1.54	2.31	1889 - 1893
49	5.07	78.9	4.66	4.41	1.62	2.41	1894 - 1898
50	5.23	92.1	3.22	4.51	1.76	2.54	1899 - 1902
51	5.31	91.3	5.02	4.66	1.86	2.47	1903 - 1906
52	4.85	112.0	5.43	4.59	1.99	2.54	1907 - 1909
53	4.24	111.0	6.43	4.69	2.32	2.77	1910 - 1912
54	4.40	105.0	6.68	4.73	2.57	2.91	1913 - 1913
55	4.78	112.0	6.95	4.68	2.51	2.89	1914 - 1916
56	5.15	123.0	6.27	4.68	2.42	2.81	1917 - 1919
57	5.00	125.0	7.80	4.75	2.55	3.00	1920 - 1923
58	4.47	150.0	9.20	4.79	2.55	3.05	1924 - 1927
59	5.00	148.0	10.65	4.59	2.31	2.94	1928 - 1931
60	6.67	154.0	10.29	4.46	2.23	2.90	1932 - 1933

TABLE I (continued)

SAMPLE NUMBER	δ_{13} ppt	δ_D ppt	δ_{18} ppt	T_{Eng} °C	T_{Basel} °C	T_{Geneva} °C	DATE SPAN
61	7.05	166.0	9.69	4.65	2.29	2.95	1934 - 1934
62	7.05	161.0	9.37	4.35	2.10	2.85	1936 - 1938
63	7.05	155.0	9.12	4.42	2.10	2.92	1939 - 1941
64	7.20	159.0	9.32	4.43	2.17	2.95	1942 - 1943
65	7.50	159.0	9.33	4.41	2.38	3.14	1944 - 1945
66	7.66	154.0	7.20	4.41	2.50	2.98	1946 - 1947
67	7.96	156.0	6.15	4.30	2.55	3.34	1948 - 1950
68	10.31	108.0	9.89	4.24	2.19	2.95	1951 - 1954

Average standard deviation on each 9 sample average of δ_{18} = 0.31 ppt

Average standard deviation on each 9 sample average of δ_{13} = 0.21 ppt

TABLE I

Nine sample running averages for measured δ_{13} and δ_{18} vs. year of center of the sample and vs. official average winter temperatures (Jan., Feb., March) in England and Basel and Geneva. Temperatures for Geneva for 1759 - 1783 (shown in parentheses) were not recorded and have been chosen by normalizing to Basel temperatures.

TABLE II – Temperature coefficients computed from measured isotope ratios and weather records.

EXPERIMENTAL TEMPERATURE COEFFICIENTS** Computed by correlating* the isotope ratios with official[6,7] average winter temperatures (averaged over January, February and March).		
ISOTOPE RATIO	TEMPERATURE COEFFICIENT	Number of Samples
$\dfrac{O^{18}}{O^{16}}$	$+ [(5.29 \pm 0.68)T_{England}]ppt$	68
	$+ [(2.91 \pm 0.41)T_{Basel}]ppt$	56
	$+ [(2.86 \pm 0.52)T_{Geneva}]ppt$	56
$\dfrac{C^{13}}{C^{12}}$	$+ [(2.73 \pm 0.67)T_{England}]ppt$	68
	$+ [(2.01 \pm 0.37)T_{Basel}]ppt$	56
	$+ [(2.37 \pm 0.41)T_{Geneva}]ppt$	56
$\dfrac{D}{H}$	$+ [(89.5 \pm 16.0)T_{England}]ppt$	68
	$+ [(67.4 \pm 6.4)T_{Basel}]ppt$	56
	$+ [(71.4 \pm 8.2)T_{Geneva}]ppt$	56

Temperature Coefficients in $(ppt) \cdot (^{o}C)^{-1}$

*The Bio Medical Data Processing Program[20] obtained from the UCB computer department, courtesy of Dr. James Enstrom, was used to correlate the isotope ratio measurements with the official air temperatures.

**These temperature coefficients were evaluated using 9-sample running averages of the measured isotope ratios. We have also correlated the 1-sample data with temperature by least squares to show that the values of the coefficients are not strongly dependent on the method of averaging, although the associated errors are larger as expected. For example, from correlation with $T_{England}$, the temperature coefficients from 1-sample data are found to be $(5.87 \pm 2.14)ppt/^{o}C$ for oxygen, $[2.71 \pm 1.50]ppt/^{o}C$ for carbon, and $(100 \pm 37)ppt/^{o}C$ for hydrogen.

TABLE III - Comparison of measured temperature coefficients with those

computed assuming formation of cellulose at equilibrium.

COMPARISON OF MEASURED and COMPUTED* TEMPERATURE COEFFICIENTS OF CARBON AND OXYGEN IN TREE RINGS IN PARTS PER THOUSAND PER DEGREE CENTIGRADE.		
	Computed* Assuming Equilibrium	Measured in this Paper**
for exchange of O^{18} between water and cellulose	0.36	
for exchange of O^{18} between atmospheric oxygen and cellulose	0.96	3.7 ± 0.5
for exchange of O^{18} between CO_2 and cellulose	1.14	
for exchange of C^{13} between CO_2 and cellulose	0.36	2.4 ± 0.4
for exchange of D between water and the O-H bond in cellulose	2.0	
for exchange of D between water and the C-H bond in cellulose	0.4	76 ± 10

*The computed values, taken from Reference 1, refer to isotope exchange at equilibrium and therefore represent lower limits of the real values of exchanges which may depend on dynamic effects. The measured values are larger than the computed values and thus must include dynamic effects, and effects from formation of rain water.

**It is known that for a water plant, Euglena, that 90% or more of the oxygen bound in cellulose comes from water, (Reference 12). The source of oxygen in trees has not been determined, but probably is the same.

Figure 1 - Photograph of tree slice

C-30
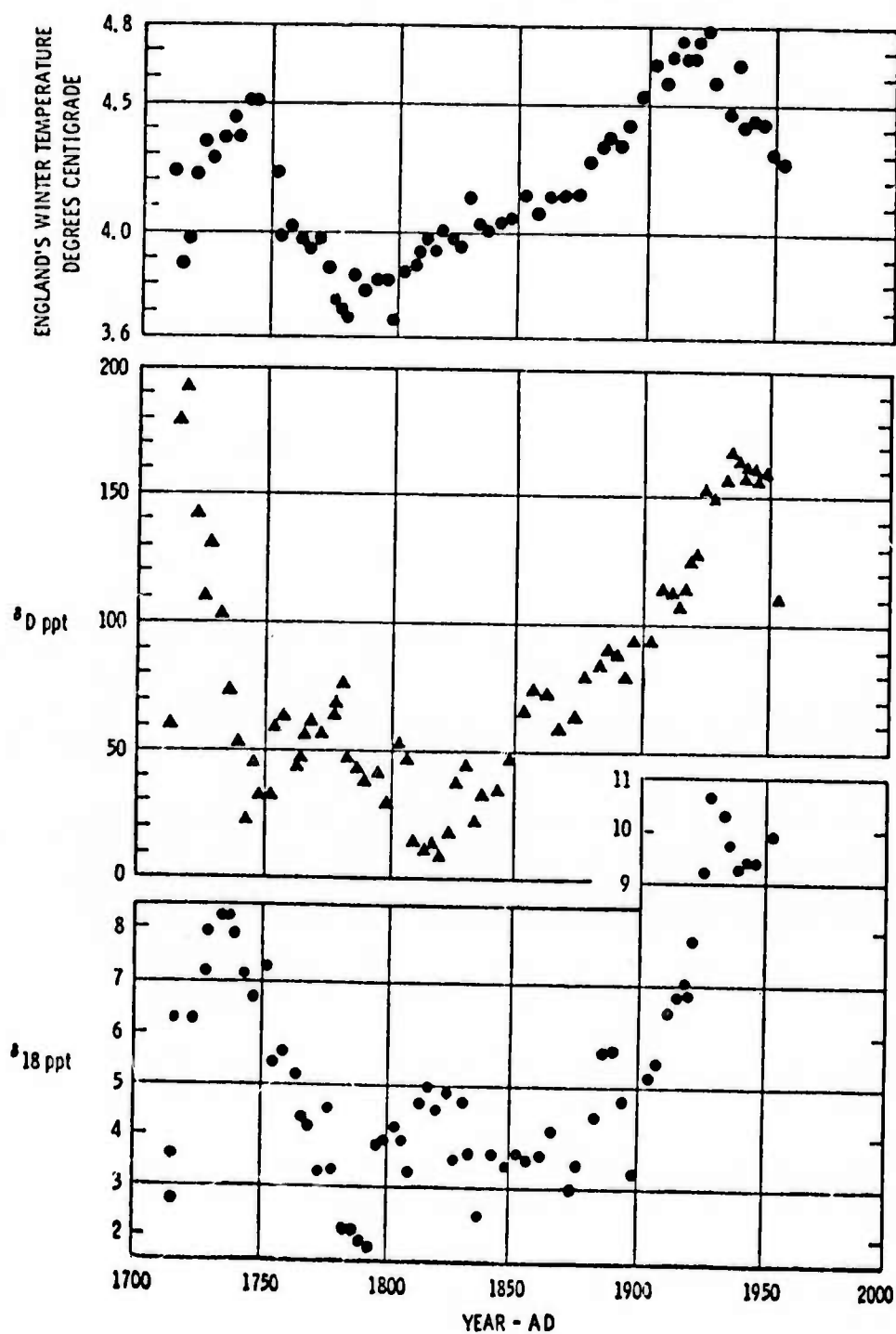
FIGURE 2a

Figure 2 — Plots of δ^{18}, δ^{13}, δ_D, and winter temperatures vs. date.
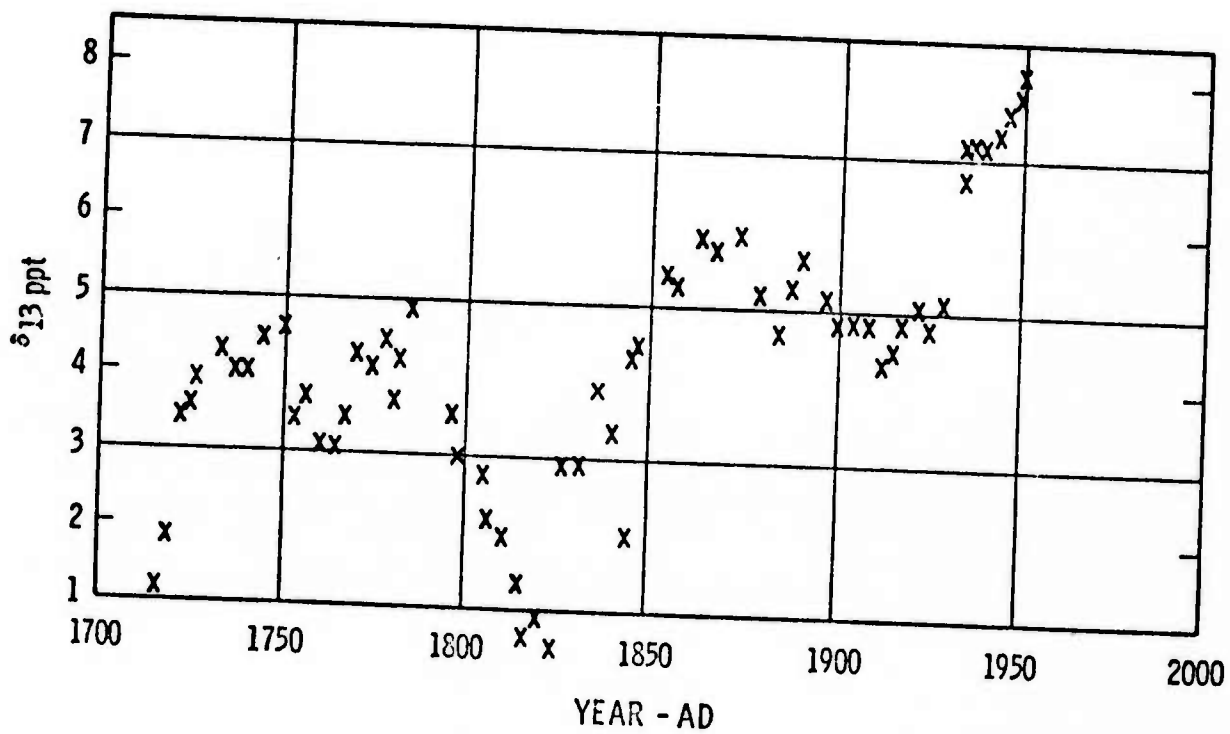
FIGURE 2b
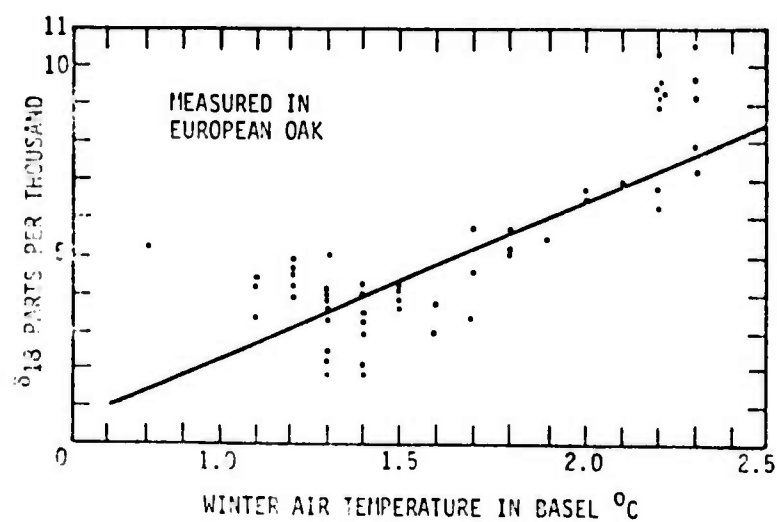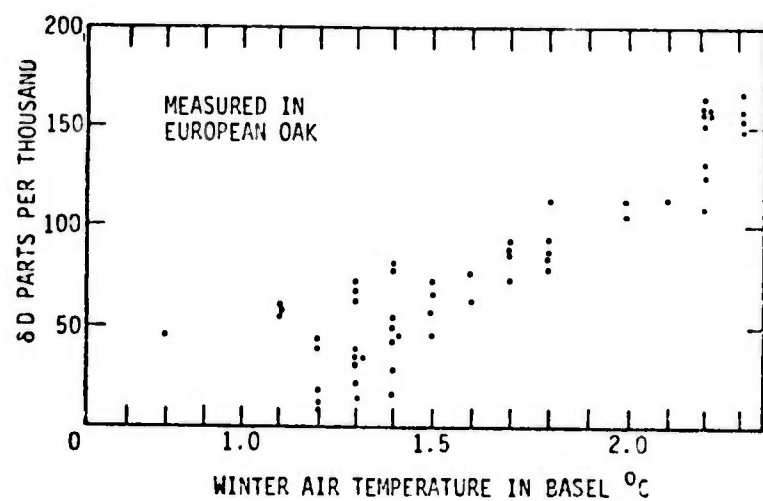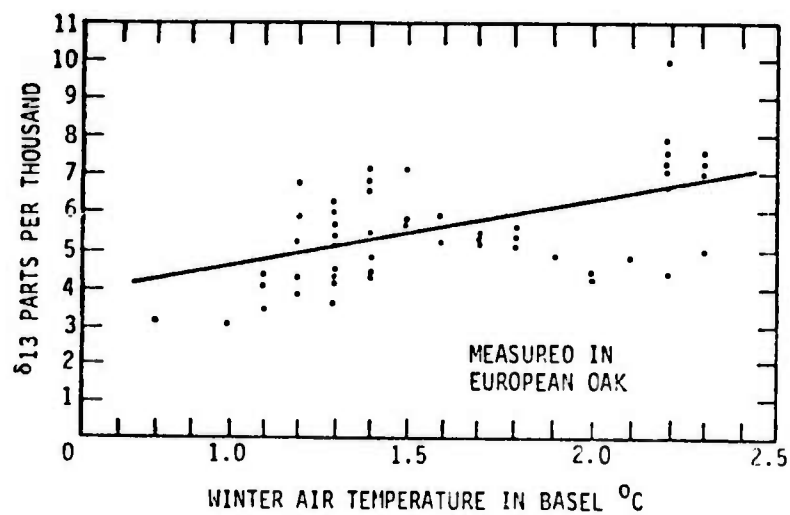
Figure 3 — Plots of δ^{18}, δ^{13}, δ_D vs. winter temperature in Basel.

-400

-350

(1953 – 1963)
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1969
ENVIRONMENTAL ISOTOPE DATA NO 1; WORLD SURVEY
OF ISOTOPE CONCENTRATION IN PRECIPITATION, 1953 – 1963
TECHNICAL REPORT SERIES NO. 96

-300

-250

-200

δ (D/H) IN PARTS PER THOUSAND

-150

D/H

-100

(+3°C, C. TAYLOR)

$D = 7.795 (O^{18}) + 4.14$

-50

0

+50

+100

+10   +5   0   -5   -10   -15   -20   -25   -30   -35   -40   -45   -50

$\delta (O^{18}/O^{16})$ IN PARTS PER THOUSAND
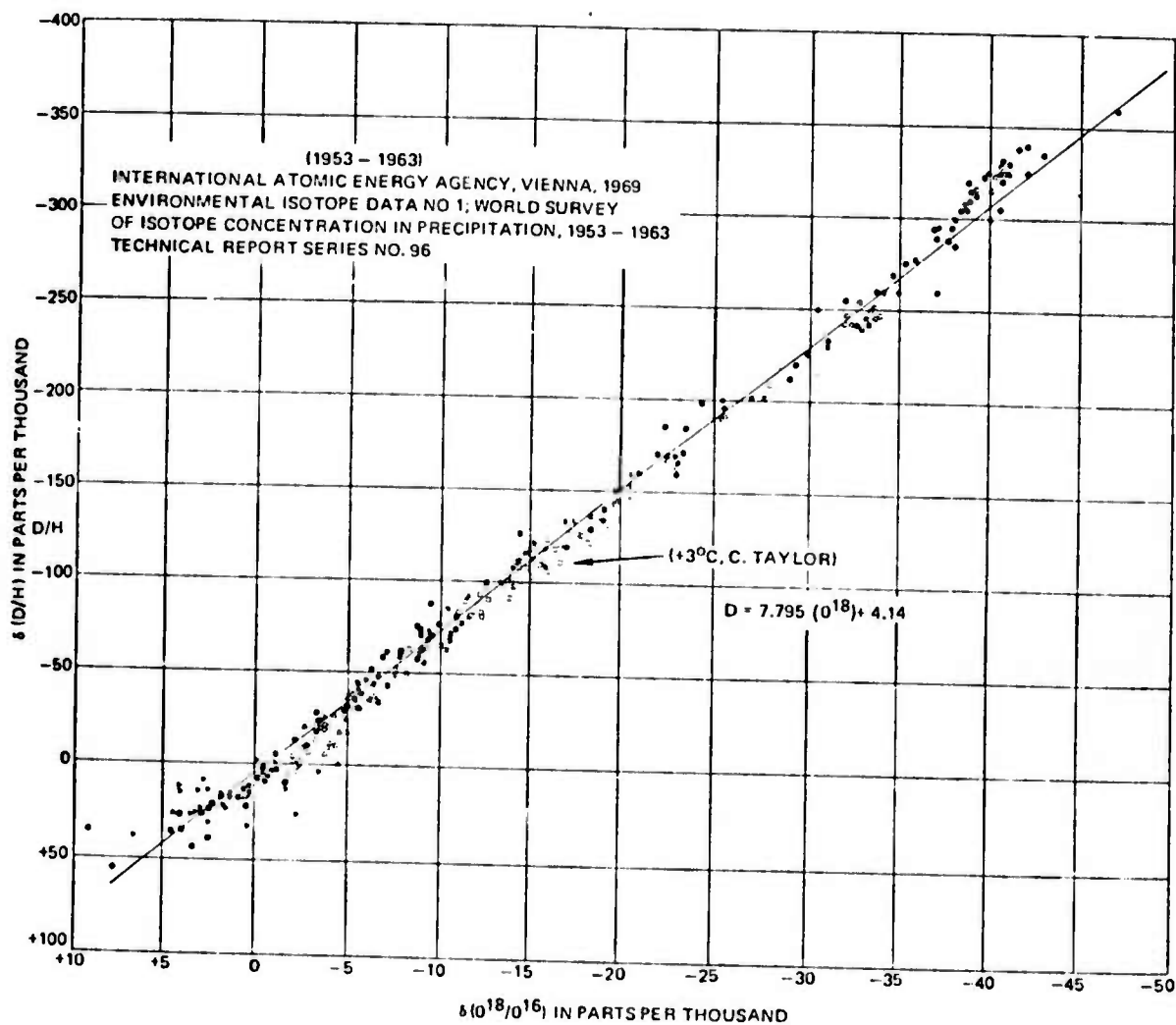
Figure 4 - Plot of δ_D vs. δ_{18} in rain and snow using data from Reference 15.
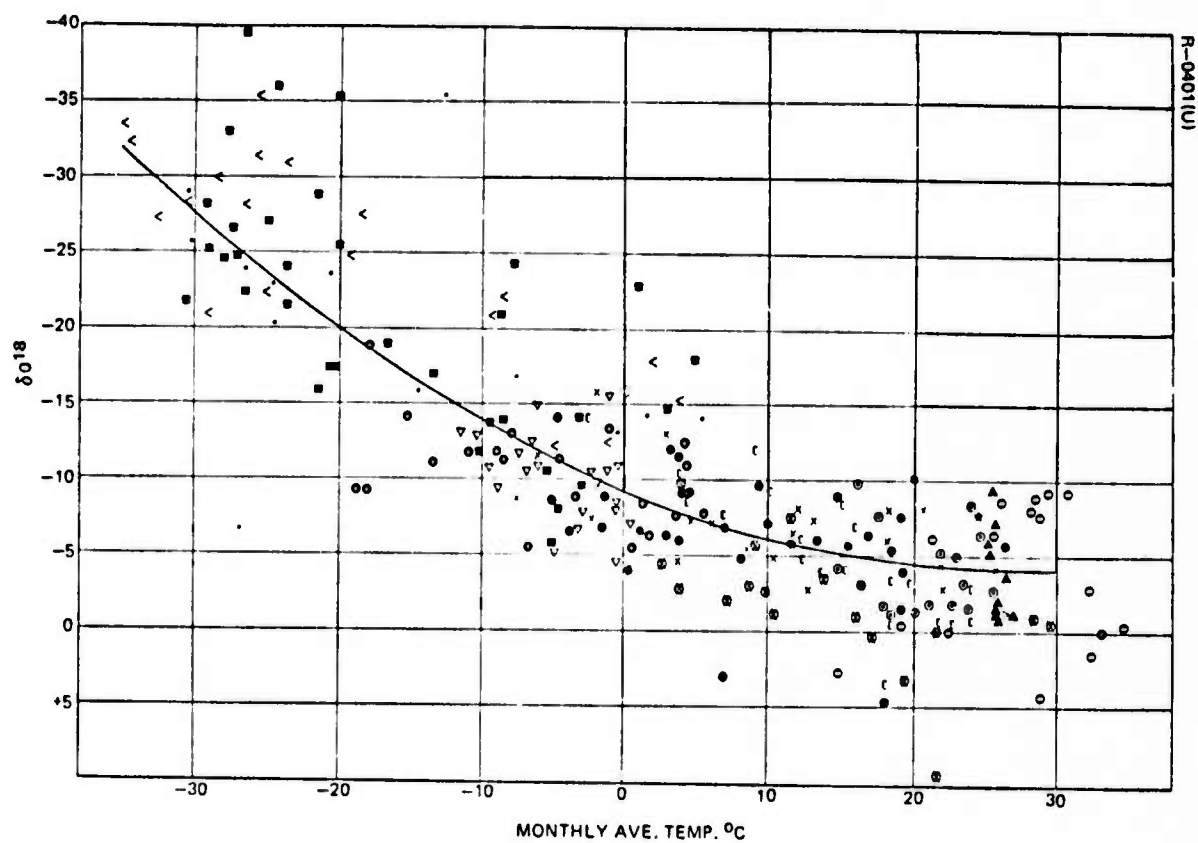
Figure 5 — δ^{18} vs. T°C at ground level using data from Reference 17.
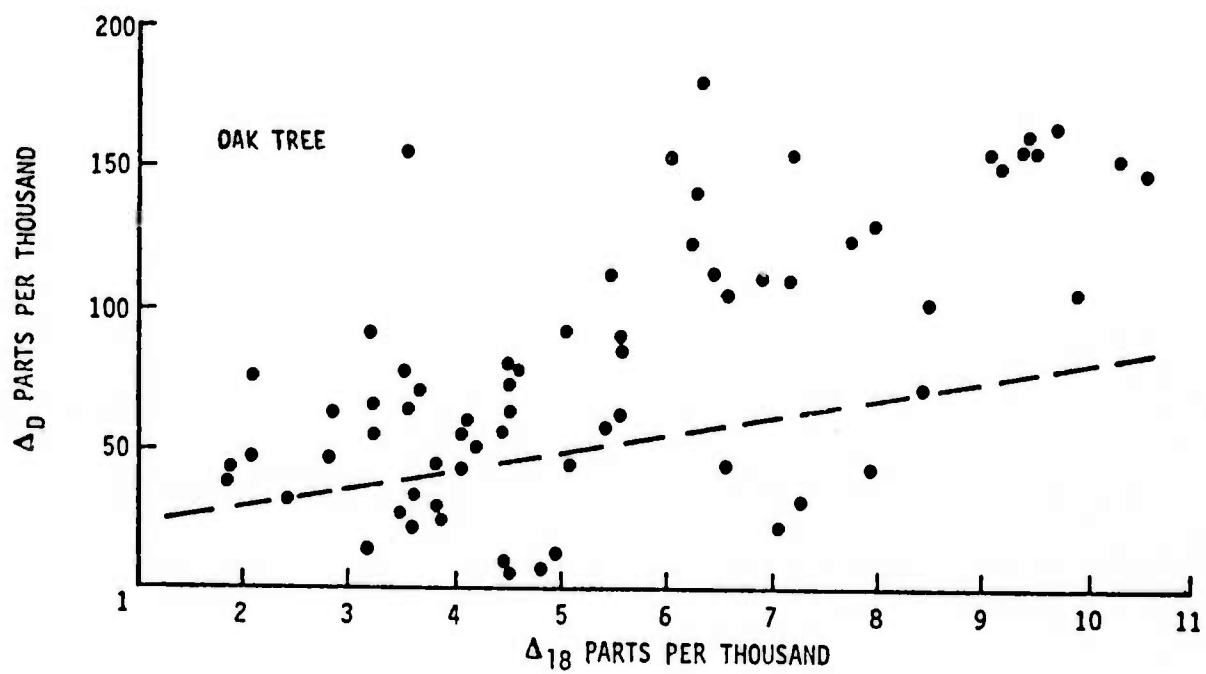
Figure 6 - Plot of δ_D vs. δ_{18} in the tree rings.

APPENDIX D

VULCANISM AND RADIOCARBON DATES

PROCEEDINGS OF 8th INTERNATIONAL CONFERENCE ON RADIOCARBON DATING

WELLINGTON, LOWER HUTT CITY, NEW ZEALAND, 18-25 OCTOBER, 1972

VULCANISM AND RADIOCARBON DATES

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ABSTRACT

We consider whether the long term perturbation of radiocarbon dates,
which is known to be approximately a sin function of period about 8000
years and amplitude of about 8% peak-to-peak, could have been caused in
any major part by vulcanism. We conclude that this is not the case.
On the contrary, present day volcanoes are a far less important source
of inert CO_2 (about 100 fold less) than is man's burning of fossil fuels
which has caused the Suess dilution of about 2%.

I. Introduction

The emission of CO_2 by volcanoes could, in principle, reduce the
concentration of radiocarbon in atmospheric carbon dioxide and thus
produce errors in the radiocarbon dates for the past millenia. However
the corrections are opposite in sign to the effects that are substantiated
by the geologic evidence. Namely, the volcanic explanation would require
that over the last eight millenia, volcanic activity would have had to
increase substantially up to the present, contrary to the geologic
evidence. Considerable evidence about the nature of such effects is at
hand from the studies of the perturbations of the radiocarbon age caused
by the burning of fossil fuel and consequent emission of carbon dioxide,
which like volcanic gases, contains no radiocarbon.

II. Material Balance

As first suggested by Suess[1], the CO_2 generated by combustion of
fossil fuels in the period 1850-1950 A.D. would have reduced the C^{14}/C^{12}
ratio in the atmosphere by a full 10% had all the fossil CO_2 remained in
the atmosphere. The actual observed dilution is $2.0 \pm 0.3\%$. This smaller
effect most likely is caused by the relatively short residence time of
CO_2 in the atmosphere before absorption into the sea, a time variously
estimated as being between 10 and 30 years[1,2]. In the time of 100 years,
which is much longer than the mixing time, most of the fossil CO_2 will
have dissolved in the sea.

Over the last 100 years, the rate of injection of fossil CO_2 increased approximately exponentially with a mean life of about 34 years. For an aggregate[3] total of 10% increase above the natural level. Today the rate of injection is 660.10^{-6} gms C per cm^2 year.

We may compare this to the average rate of outgassing of carbon dioxide over geologic time. Rubey[5] estimates the total carbon in terrestrial sediments as 9.10^{22} gm or 2.10^4 gm/cm^2. This is in agreement with the quantity of atmospheric CO_2 observed on Venus[6]; (supposing that sediments cannot form on Venus because of the lack of oceans[7], then the total CO_2 outgassed in the life of Venus is still all in the atmosphere). Some 100 atmospheres[6] of CO_2 correspond to 3.10^4 gm C/cm^2, about the same as the total outgassed on the earth. Thus the average rate of evolution for either planet is then approximately 6.10^{-6} gm/cm^2 yr for the lifetime of $4.5 \cdot 10^9$ yr. This is about one percent of the rate of evolution from fossil fuel. Thus volcanoes would have to increase their activity by some 100 times more than the average, and do so in a smooth way, sinusoidally dependent on time, to have caused the observed corrections for radiocarbon dates.

We may approach the problem in another way. Namely, B.E. Nordlie[9] has analyzed the volcanic emissions from Kilauea in Hawaii and found them to be approximately 33% CO_2 by volume. We assume that this gas contains only inert carbon. An estimate of world-wide lava production of 1 km^3 per year has been made by G.C. Kennedy[10]. At production the lava has a density of about 3, and decompresses to pumice of density about 1, with emission of about 2 km^3 of gas. When corrected to NTP (the gas is emitted at about $1100°C$) the CO_2 emitted totals about $4 \cdot 10^{-8}$ gm C/cm^2 yr at this postulated level of vulcanism. This again is very small compared with the present rate of injection of inert CO_2 from fossil fuel injection and could have caused no serious effect on radiocarbon dates.

Finally strong evidence exists that vulcanism reached its greatest intensity early in earth's history and has been decreasing since[5]. Thus the present world-wide average should be much less than one percent of the present fossil fuel combustion rate.

III. Conclusions

Our conclusions are as follows: (1) there is evidence that vulcanism in the last eight millenia has been too inactive to have caused a noticeable correction in radiocarbon dates. In fact the evidence is that vulcanism reached its greatest intensity early in the earth's history and has been decreasing since[5]. (2) At present, volcanoes appear to be evolving one percent or less of the CO_2 being evolved by burning fossil fuel.

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APPENDIX E

PRODUCTION OF RADIOCARBON IN TREE RINGS BY LIGHTNING BOLTS

Production of Radiocarbon in Tree Rings by Lightning Bolts

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Lightning bolts appear to be able to produce neutrons by processes associated with the acceleration of ions to an amount estimated to be about a percent of the cosmic ray neutron production. The corresponding effect on radiocarbon in tree rings can explain the well-known short-term secular errors in radiocarbon dates as being caused by climatological fluctuations in frequency of lightning storms.

The short-term secular variations of radiocarbon in tree rings have a time scale of about 100 years and an average amplitude of a few percent. They have been attributed to fluctuations in the solar cosmic ray intensity [*Suess*, 1965]. The likelihood that they could have been caused by changes in the volume of volcanic emissions has been discounted [*Libby and Libby*, 1972].

In the present communication we discuss ^{14}C production in thunderstorms and show that its present day magnitude may be a few percent of ^{14}C production by cosmic rays, so that hundred-year fluctuations in the frequency of thunderstorms could explain the short-term secular variations in radiocarbon in tree rings.

Neutrons have been observed to be produced in laboratory electric discharges; therefore it may be that they are produced in natural discharges, namely, lightning bolts.

In a lightning storm, as described by *Loeb* [1954], there are electric fields up to 1500 volts/cm giving rise to lightning bolts 10^5 kw hours in magnitude, with average electron energy of ~ 150 kev. If a Boltzmann distribution is assumed, a finite fraction (10^{-6}) of electrons have energies greater than 2.2 Mev, and a much smaller fraction (10^{-23}) of electrons have energies greater than 8 Mev. Furthermore, other acceleration mechanisms, chiefly pinch effect,

seem to be operating and thus producing copious quantities of neutrons of ~ 2.5 Mev, according to experimental observation.

In an experiment [*Stephanakis et al.*, 1972] in which electric discharges were created between electrodes connected with nylon threads, the nylon exploded; electrons and heavy ions, which were accelerated to approximately equal energies, on the average about 10 kev, and neutrons of about 2.5 Mev were produced. Nylon threads enriched in deuterium, when they were similarly exploded, produced copious 2.5-Mev neutrons from the d-d reactions; thus it was shown that the heavy ions were being accelerated. The yield of 2.5-Mev neutrons from exploded hydrocarbon threads of natural hydrogen abundance was determined as about 10^8 neutrons for an electric discharge of 14 watt hours, in a discharge a few centimeters long.

For a lightning bolt of 10^5 watt hours [*Loeb*, 1954, p. 348] the number of neutrons is expected to be 10^{12}. Specifically, this production is arrived at as follows.

The yield Y of neutrons in a pinch is expected to vary as the square of the density N of ions and as the volume V and lifetime τ of the pinch, so that

$$\frac{Y_l}{Y_w} = \left(\frac{N_l}{N_w}\right)^2 \frac{V_l}{V_w} \frac{\tau_l}{\tau_w}$$

where the subscripts l and w designate light-

E-2

ning bolts and exploding wires, respectively. We take $\tau_l = 500$ μsec, $\tau_w = 50$ nsec, $N_l \sim 10^{-3}$ g/cm³, $N_w \sim 1$ g/cm³, $V_l \sim 10^{-7}$ cm³, and $V_w \sim 10^{-1}$ cm³, from which it follows that $Y_l/Y_w = 10^8$. If $Y_w = 10^8$, then $Y_l \sim 10^{16}$.

On the average around the world, R. E. Holzer (private communication, 1972) has evaluated the total number of lightning bolts per second to be between 100 and 300, which, if Loeb's calibration of lightning bolts is assumed, would lead to an estimate of about 1×10^{18} to 3×10^{18} neutrons created in the atmosphere per second over an area of 5×10^{18} cm². Holzer warns that this calibration is probably too high by at least a factor of 10. We therefore reduce it by this factor and arrive at a neutron production from storms of (2–6) $\times 10^{-3}$ neutrons/cm² sec, as compared with the cosmic ray production of 2.6 neutrons/cm² sec, or a perturbation of about 1%.

Suess notes that a comparison of recent radiocarbon fluctuations in tree rings with sunspot numbers since 1000 A.D. suggests that a correlation exists between them. It is not unreasonable that frequency of thunderstorms should be correlated to sunspot numbers and should modulate the production of atmospheric radiocarbon by electric discharges; thus the correlation found by Suess in tree rings would be explained.

It is barely possible that an enhancement of radiocarbon in trees on a mountain ridge frequently struck by lightning could be measured. The natural rate of ^{14}C decay is 15 dpm/g C, corresponding to a content (taking the lifetime as 8265 years or 4.1×10^9 min) of 6×10^{10} ^{14}C atoms/g C. Let us ask for a 1% perturbation, namely, that 6×10^8 ^{14}C atoms/g C be produced by lightning; in dense dry (dead) wood, this corresponds to 2×10^8 ^{14}C atoms/g wood.

The nitrogen content of such wood is about 2×10^{-3} by weight. Neutrons entering wood are captured either by hydrogen or by nitrogen. The fraction captured by nitrogen is given by

$$F = A_N \sigma_N/(A_N \sigma_N + A_H \sigma_H)$$

where A_N and A_H are the atomic fractions of N and H and where $\sigma_N = \sigma_N(n^{14}N \rightarrow p^{14}C) = 1.7 \times 10^{-24}$ cm² and $\sigma_H = \sigma_H(nH \rightarrow \gamma D) = 0.3 \times 10^{-24}$ cm².

Taking the schematic formula for wood to be CH_2O and considering capture in a fallen tree with negligible water content, such as Bristlecone, we find that $F \sim 0.02$.

To create 1% excess of ^{14}C in wood then requires capture of 10^{10} neutrons/g wood, or 10^{16} neutrons in a tree weighing a ton. Thus, to produce this amount, several hundred lightning bolts must strike nearby trees and rocks. It follows that fallen trees on an exposed ridge where electrical discharge is common in every storm just might show this enhancement. This ^{14}C may be chemically separable from cellulose and lignin, since the hot atom chemistry of carbon is unlikely to introduce the ^{14}C into these molecules without shattering them. This possibility could be checked by irradiating wood with neutrons.

A caution should be added that the foregoing estimates of ^{14}C production may be in error in either direction. Namely, the value of the average lightning bolt energy [Loeb, 1954] we have used although it was decreased by a factor 10 may still be too high. On the other hand, the numbers of neutrons observed in experimental discharges [Stephanakis et al., 1972] scatter over a range of up to 5×10^8 neutrons of 2.5 Mev, and there may be much larger numbers of lower-energy neutrons produced, all of which are able to produce ^{14}C by capture into nitrogen.

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APPENDIX F

GLOBALLY STORED ORGANIC CARBON AND RADIOCARBON DATES

Globally Stored Organic Carbon and Radiocarbon Dates

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When recent data on the rate of addition of CO_2 to the atmosphere as a result of bacterially caused decay of organic carbon produced by the biosphere are used, it is found that variations of climate acting on the biosphere can cause fluctuations of up to 100 years in amplitude in the corrections to radiocarbon dates.

This paper discusses the effect on radiocarbon dates of variations in the amount of carbon stored globally as organic material that originated in the biosphere. Using new measurements of global evolution of CO_2 from the decay of stored organic carbon, we find that the short-term 'wiggles' [*Suess*, 1970] in the amount of radiocarbon in tree rings, of an amplitude of about 100 years peak to peak, can be explained. The present discussion updates and quantifies the original treatment of this subject by *Libby* [1952].

Discussion

In the process of making bio-organic matter, plants store carbon depleted with respect to atmospheric carbon by about 2.7% in ^{13}C [*Kroopnick et al.*, 1970; *Gordon and Williams*, 1970; *Maugh*, 1972] and therefore by about 5% in ^{14}C [*Rafter*, 1955]. If the amount of depleted carbon stored in the biosphere in the past has been different from what it is now, radiocarbon dates for the past will reflect an error. The size of error is estimated in this paper and is found to be about 100 years maximum.

The carbon in the bio-organic material withdrawn from the atmosphere and stored in the plant for the life of the plant plus an additional time of storage as dead organic carbon is eventually released by bacterial decay and returned to the atmosphere mainly as CH_4. In the atmosphere methane quickly oxidizes to CO_2 as an end product. At present the global quantity of CO_2 originating from plant decay and returned

to the atmosphere is estimated [*Maugh*, 1972] as about 1.8×10^{10} tons CO_2/yr, or 1.0×10^{-3} g C/cm^2 yr. Let the total time of withdrawal from the atmosphere be τ years. Then it follows that the amount of C presently stored as organic carbon is 1.0×10^{-3} $\tau g/cm^2$.

The storage time τ may vary depending on climate and vegetation; for example, the mean age has been found to range from 10 to 1600 years in New Zealand soil [*O'Brien and Stout*, 1972]. The mass of organic carbon is mainly in the oceans, however. The average concentration of dissolved organic carbon in the oceans is measured [*Menzel and Ryther*, 1970; *Holm-Hansen*, 1970] as about 500 $\mu g/l$ or 0.5 μg C/g sea water. When the average depth of the oceans is taken as 2800 meters, it follows that 0.14 g organic C/cm^2 is stored as dissolved material.

Since 1×10^{-3} g C/cm^2 is returned to the atmosphere per year [*Maugh*, 1972], the average storage time is about 140 years.

An independent estimate of the storage time comes from the following biological argument. More than 98% of all organic carbon in the oceans is dissolved organic carbon, at about 500 $\mu g/l$ [*Holm-Hansen*, 1970]. The total quantity of this dissolved organic carbon in the entire depth of the ocean represents about 100 times the average annual production of organic carbon in the sea surface. The annual production is known quantitatively to just be able to satisfy the metabolic requirements of the grazing population [*Menzel and Ryther*, 1970]. Thus the total organic carbon in the oceans is the amount presently produced in about 150 years and is in steady state, being eaten and re-eaten, the final state being gases produced by bacterial action. The chemical estimate of 140 years and

F-2

the biological estimate of about 100 years are in reasonable agreement.

In comparison, Libby [1952], in explaining the fundamentals of radiocarbon dating, arrived at an inventory of 0.33 g organic C/cm². His estimate, made 25 years ago, was remarkably close to the above estimate of 0.14 g C/cm² derived from new data.

The total atmospheric CO_2 is about 2.33×10^{12} tons, or 0.13 g C/cm². The value of the atmospheric residence time before absorption into the seas has recently been updated [Gullikson and Nydal, 1972] to about 8-12 years. In the absence of universal agreement, for convenience, we round it off here as 10 years. Then 2.3×10^{11} tons, or 0.013 g C/cm², are exchanged with the oceans each year.

In past times the total mass of stored organic carbon may have been larger or smaller than it is now, depending on the climate. Let us define as the norm the amount of carbon presently stored and define a time dependent factor α by which the organic carbon reservoir may be increased $(\alpha > 1)$, as in a lush, tropically global coal age, or decreased $(\alpha < 1)$, as in an ice age. We assume that the total atmospheric CO_2 has always remained the same.

Since the organic carbon reservoir is about 5% depleted in radiocarbon, the atmospheric reservoir is correspondingly enriched by about 5% multiplied by the ratio of the mass of stored organic carbon to the total carbon in both reservoirs, namely, the atmosphere and the organic reservoir. That is, the enrichment ϵ is given by

$$\epsilon = 0.05\{0.14\alpha/[0.13 + 0.14(1 - 0.05)\alpha]\}$$

$$\epsilon = 0.05[\alpha/(0.95\alpha + 0.93)] \qquad (1)$$

where α is the ratio of the mass M of organic carbon at the time when the material was alive to the mass M^* in the year 1972 A.D.; $\alpha = M/M^*$.

The enrichment ϵ can be positive or negative with respect to the present. Now in 1972 A.D. we define $\alpha = 1.0$ and $\epsilon = \epsilon^* = 0.0266$. The error in the radiocarbon date with respect to the norm is given by the enrichment difference times the mean radiocarbon lifetime of 8268 years:

$$\text{error} = (\epsilon - \epsilon^*) \times 8268 \text{ years} \qquad (2)$$

The age correction depends on the numerical value of 5% depletion of ^{14}C in plants in comparison with CO_2 in the atmosphere. This quantity in turn depends on the temperature T at which the bio-organic material grew and itself has a temperature coefficient. The coefficient for $^{14}C/^{12}C$ in marine plankton has been measured as 0.35 ppt/°C [Be et al., 1965] and independently as 0.5 ppt/°C [Eadie, 1972]. It may be the same or larger for the average of all plants [Libby, 1972]. In the absence of more measurements we assume it to be the larger of the two experimental values, namely 0.50 ppt/°C, because it seems unlikely that the true value is exactly equal to the minimum value allowed thermodynamically [Libby, 1972], which is 0.35 ppt/°C.

Then, on the basis of the foregoing assumptions, the temperature coefficient will be 1.0 ppt/°C, so that, if the climate were much warmer, say, by 10°C, the ^{14}C depletion of the stored organic carbon would decrease from 0.050 to 0.040, corresponding to an age correction of $(0.050 - 0.040) \times 8268$ years, or 83 years too old. Similarly, if the temperature fell 10°, the depletion would increase to 0.060, corresponding to an age correction of 83 years too young, even without any change in the mass of the biosphere, the dependence on which is set forth in (2).

But still another effect enters: that caused by the presence of ocean carbonate. The sea contains dissolved carbonate that is fractionated in $^{14}C/^{12}C$ in comparison with that in the atmosphere, the amount of dissolved carbonate depending on the temperature at the sea-air interface. Sea carbonate is enriched in ^{14}C with respect to atmospheric CO_2 and is less so as the temperature increases, so that the result is to provide a small correction that partly cancels the effect of fractionation in stored organic carbon.

This perturbation comes only from carbonate in the ~100-meter-thick surface mixed layer of the ocean that contains [Craig et al., 1972] about 0.15 g C/cm², which is approximately equal to that in the atmosphere and to that in the organic carbon dissolved in the total depth of the sea. In the case of organic carbon the total depth of the sea is involved because bacterial decomposition occurs at all depths, producing CH_4 and CO with which the sea water is saturated, so that these bacterial

gases are bubbling up from all depths. In comparison, the sea is not saturated with CO₂ at any depth [*Craig et al.*, 1972].

Carbon isotope fractionation by CO₂ absorption at the air-water interface has been measured [*Degens and Deuser*, 1967], and the ratio ¹³C/¹²C has been found to vary from 9.2 to 6.8 ppt over the temperature range 0°–30°C. The corresponding fractionations of ¹⁴C/¹²C versus temperature are shown in Table 1 and are obtained by multiplying the fractionation of ¹³C/¹²C by 2.

The corrected enrichments (or depletions) of ¹⁴C/¹²C in the atmosphere for climates 10°C warmer (or colder) than those at present are given in Table 2, where it is assumed that the average global temperature at present is 20°C. The corrections caused by ocean carbonate are shown to be about 20% of the temperature variations of ¹⁴C/¹²C in organic carbon and of opposite sign.

The equation including both corrections can now be written

$$\epsilon = n\alpha/[(1 - n)\alpha + 0.93]$$
$$n = [0.05 - 8.5 \times 10^{-5}(T - T^*)]$$

(3)

The computed corrections are shown in Table 2 to be of the order of ±50 years, namely, of a total amplitude of about 100 years.

We conclude that the experimentally determined fluctuations in the correction curve for radiocarbon dates [*Suess*, 1970] as determined in tree rings may be caused by changes in the climate that perturb the storage mechanism discussed here. A short period of climate either

TABLE 1. Corrections Caused by Fractionation of ¹³C in Surface Ocean Carbonate and in Dissolved Organic Carbon Versus Average Temperature of the Sea Surface, α

Sea Carbonate in Mixed Layer	Dissolved Organic Carbon in Sea	Temperature, °C
1 + 0.0186*	1 - 0.070	0
1 + 0.017	1 - 0.060	10
1 + 0.0154	1 - 0.050	20
1 + 0.0138	1 - 0.040	30

α is the ratio of (¹⁴C/¹²C) in aqueous carbonate to (¹⁴C/¹²C) in atmospheric CO₂.
*As given by *Craig et al.* [1972].

TABLE 2. Corrections to Radiocarbon Dates in Bio-Organic Materials as a Function of Average Temperature and Biomass

α = M/M*	Correction, years		
	10°C	20°C	30°C
0.5	-48	-73	-111
1.0	38	0	-40
2.0	127	73	18
∞	296	214	144

Corrections assume that the changed climate endures for 100 years or more and include the corrections caused by ocean carbonate in the mixed layer of the sea.

warmer or colder than that at present could cause the atmospheric radiocarbon to differ from the norm, with a corresponding error, positive or negative, in radiocarbon dates of bio-organic material for those periods. By short is meant periods of time about as long as the average storage time of about 100 years. This storage time itself might have changed with time if the oceans had changed, but the temperature of the sea below the thermocline is only slightly above 4°C and the time of overturn is about 1000 years, so that no significant change could have occurred in the last 8000 years, the period for which the fluctuations in tree ring radiocarbon have been measured.

Support for the hypothesis of a fluctuation in the amount of stored organic carbon in the past is suggested by measurements on CO in the Greenland and Antarctic icecaps [*Cavanagh et al.*, 1972]. Specifically, these measurements find concentrations of CO as high as 0.3 ppm in air trapped in the ice for ice samples up to 2500 years old, whereas modern CO concentrations in clean air, remote from cities, are 0.04–0.20 ppm at ground levels [*Jaffe*, 1972] and 0.08 ppm at a 4-km altitude and decrease to 0.04 ppm at a 15-km altitude [*Bradford*, 1972] Since the largest global source of CO is oxidized methane, these measurements suggest that the reservoir of stored bio-organic material has varied in the past.

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APPENDIX G

MULTIPLE THERMOMETRY IN PALEOCLIMATE AND HISTORIC CLIMATE

Multiple Thermometry in Paleoclimate and Historic Climate

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The principle of isotope thermometry is that isotope ratios are temperature dependent. It is proposed that isotopic ratios in bio-organic material may have independent temperature coefficients, so that, by measuring ratios for several elements, e.g., hydrogen, carbon, and oxygen, it may be possible to show that a temperature change occurred. Assuming that cellulose is formed almost at equilibrium, temperature coefficients for C, H, and O are computed and found to be of measurable size. The coefficients computed for $^{13}C/^{12}C$ and D/H agree with measured values. Thus indications are that temperature changes in past climates can be measured in old tree rings by using this principle of multiple thermometers.

The principle of isotope thermometry is that the isotopic ratios are temperature dependent. There are two kinds of temperature dependence, kinetic and equilibrium. The theory of kinetic isotope separation is well established. For example, in the gaseous diffusion process for separation of the uranium isotopes, separation is caused by a difference in the rates with which the two species pass through holes in a barrier. In case of equilibrium, separation is caused by a difference of differences, namely the difference between separation by the forward rate and separation by the reverse rate, the two rates being equal. Distillation of liquid in a closed container is an example of separation at equilibrium, while vaporization into a vacuum is kinetic.

In distillation of a liquid containing two or more elements in the molecule, the corresponding isotope thermometers are functionally related, because the corresponding vapor-pressure ratios, which determine the separations on evaporation and condensation, depend on the same force constants tying them together.

In bio-organic material, however, there may be at least three useful isotope thermometers, namely D/H, $^{13}C/^{12}C$, and $^{18}O/^{16}O$. The basic reaction is photosynthesis with production of cellulose, here written schematically as a basic module,

$$H - \overset{|}{\underset{|}{C}} - OH \quad \text{or} \quad CH_2O$$

according to

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$
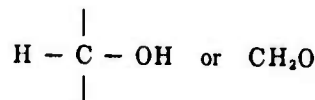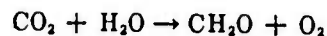
In this reaction, all three elements may yield isotope thermometers, and they may be independent of each other; that is, the ratio $^{18}O/^{16}O$ is no longer functionally related to D/H, because diatomic oxygen is being evolved, and so rotational and vibrational energies of the O-O bond are involved, and because, in cellulose, oxygen is bound to carbon as well as hydrogen. For the same reason, the temperature coefficient of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ may not be functionally related. Finally, the ratio $^{13}C/^{12}C$ should be independent of D/H, because carbon and hydrogen are initially in different molecules with different vibrational frequencies.

If variations are measured for only one isotope ratio, the relation to paleotemperature is not proved. However, if ratios are measured for two, three, or more independent isotopes in the same organic material, it is possible that the relation to temperature can be firmly established and quantified, and this is the principle point of the present discussion.

Over the small temperature interval ($0°C < t < +30°C$) within which climate could have varied without killing terrestrial life as we know

it, the dependences of isotope ratios on temperature can be assumed to be linear for bio-organic material. That is, for isotope ratios δ^j, where $j = 2, 13, 15, 18, 34, 41, \cdots$, referring to D, ^{13}C, ^{15}N, ^{18}O, ^{34}S, ^{41}K, $\cdots$, the temperature dependence can be written as

$$\delta^j = a^j t + b^j$$

(a^j and b^j constants)

where a^j is the temperature coefficient and t is temperature. Then a change Δ' is related to a change $\Delta\delta^j$ by (for a given compound)

$$\Delta t = \frac{\Delta\delta^2}{a^2} = \frac{\Delta\delta^{13}}{a^{13}} = \frac{\Delta\delta^{15}}{a^{15}} = \frac{\Delta\delta^{18}}{a^{18}} = \cdots$$

The multiple overdetermination of temperature by using a set of many thermometers may make it possible to show with some level of confidence that a temperature change did occur. It is also possible that new effects, not caused by temperature, will be demonstrated by the method of multiple thermometry, if some of the above ratios, but not all of them, show equality. Probably the specific relations to temperature will have to be calibrated at each geographical position to take into account local variations in water and CO_2.

Finally, bio-organic data bases can be radiocarbon dated, so that, if evidence for temperature changes is stored in them, the dates when the changes occurred can be evaluated.

EXPERIMENTAL EVIDENCE FOR TEMPERATURE DEPENDENCE OF ISOTOPE RATIOS IN BIO-ORGANIC MATERIAL

Although animal bio-organic material is not directly derived from photosynthesis, nevertheless animals are largely what they eat, so that bio-organic material from both plants and animals may be useful in isotope thermometry. Some of the evidence [Craig, 1953] on isotope thermometers in bio-organic material is as follows.

The ^{13}C/^{12}C ratio in combustible organic matter in cores from sea bottoms shows variations of as much as 6 ‰ with depth. These have been measured and attributed to temperature variation in the sea surface with time by Rogers and Koons [1969]. Also, in a study of marine plankton [Sackett et al., 1965] the ^{13}C concentration was found to be depleted by 6 per mil

where surface waters are near 0°C relative to samples collected where surface temperatures are about 25°C. These observations on both plant and animal plankton suggest that the temperature coefficient of ^{13}C/^{12}C in bio-organic material is $\sim 0.24‰/°C$ in the temperature range 0°–25°C.

In further work [Degens et al., 1968], the temperature coefficient of ^{13}C/^{12}C in marine phytoplankton grown in laboratory cultures was measured as $\sim 0.35‰/°C$ between 10° and 30°C.

Although shell carbonate is not, strictly speaking, bio-organic material, nevertheless, for completeness we note here that variations in the ^{18}O/^{16}O ratio in Foraminifera shells from Caribbean Sea cores have been measured by several workers and interpreted in terms of paleotemperature variations [Emiliani, 1966]. This, in fact, was the first isotope thermometer developed by Urey [1947].

It may be that other isotope ratios in bio-organic material are temperature dependent, such as ^{15}N/^{14}N and ^{34}S/^{32}S, perhaps increasing the number of independent thermometers in bio-organic data bases to five or six. This possibility should be investigated.

THE QUESTION OF EQUILIBRIUM

An attempt is made here to estimate the magnitudes of the temperature coefficients of the several isotope thermometers in bio-organic data bases. This can be done using thermodynamic considerations, if one assumes that the organic material is manufactured in equilibrium with its surroundings. This is of course a major assumption, but one that does not seem too unlikely. For example, in experiments in the laboratory, the isotopic composition of $CaCO_3$ slowly formed from aqueous solution was found to be the same as that in the shells produced by aquatic organisms at the same temperature [McCrea, 1950]. In any case, this assumption can be tested for plants and animals grown under laboratory conditions.

In the wild state, in coastal waters and estuaries, the carbon and oxygen isotopic composition of shell carbonate has been shown to be in isotopic equilibrium with bicarbonate dissolved in the water [Mook and Vogel, 1968]. The life span of the shell fish is about one year, so it would seem that equilibration in self-manufacture might take place rapidly, say in

less than or about a day. Equilibration between CO_2 gas and sea water is known to occur in less than 48 hours (*Li and Tsui*, 1971], and among CO_2 gas, water, and precipitated $CaCO_3$ in less than 6 days [*Bottinga and Craig*, 1969; *Emrich et al.*, 1970]. In living animals, tritiated water is known to equilibrate with blood serum of rats in 6 days or less [*Gleason and Freedman*, 1970]. Thus the evidence, although meager, is that equilibration takes place rapidly compared with the relevant life spans.

In shells, the carbon and oxygen are not independent thermometers, because they are tied by the same vibrations in the C-O bond. However, there is organic material in the shell matrix that could provide a set of multiple thermometers, and also could be radiocarbon dated.

The question of the degree to which equilibrium obtains in formation of cellulose is interesting in itself. If equilibrium seems to apply, the assumption could be extended to computations of production of other substances. If equilibrium does not obtain, and instead the processes of isotope fractionation are kinetic, then the temperature coefficients should be even larger than those estimated by assuming equilibrium.

Calculation of Partition Function for Cellulose

For a reaction in which there is isotope exchange, the equilibrium constant K_{eq} can be expressed in terms of the total partition functions $Q*$ and Q for molecules containing the heavy and light isotopes, respectively, as follows. We define Q as the product of rotational, vibrational, and translational parts, neglecting vibrational-rotational coupling:

$$Q = Q_{rot} Q_{vib} Q_{tr} \tag{1}$$

For solids and liquids, $Q_{tr} = 1$ and Q_{vib} is given by

$$Q_{vib}(T) = \sum_j \sum_n g_j \exp\left(-\nu_j n \frac{h}{kT}\right)$$
$$\exp\left(-\Delta\epsilon_j/kT\right) \quad (n = 0, 1, 2, \cdots) \tag{2}$$

which can be written as

$$Q_{vib}(T) = \Pi_j g_j [1 - \exp(-h\nu_j/kT)]^{-1}$$
$$\cdot \exp(-\Delta\epsilon_j/kT) \tag{3}$$

We shall be computing partition functions at

TABLE 1. Stretching Vibrations Assumed for Cellulose

Bond	Stretching Vibration, cm^{-1}
$-\overset{\mid}{\underset{\mid}{C}} - H$	2960
$-\overset{\mid}{\underset{\mid}{C}} - \overset{\mid}{\underset{\mid}{C}} -$	900
$-O - H$	3680
$-\overset{\mid}{\underset{\mid}{C}} - (OH)$	(1200)*
$^{16}O - ^{16}O$	1580
	$B = 1.44560$

*Calculated from a force constant taken as 1/2 of force constant for $C = O$ [*Herzberg*, 1945, p. 195, Tables 51 and 89].

$\sim 300°K$, so that the harmonic oscillator approximation is reasonably good. Here k is the Boltzmann constant, t is the absolute temperature. ν_j is the frequency of the jth appropriate vibration of degeneracy g_j, n is the vibrational quantum number, and $\Delta\epsilon_j$ is the difference in zero-point energy between the isotopes. In cellulose, the barriers preventing free internal rotation are high, so that rotations deteriorate into torsional oscillations or bending vibrations. In the present treatment, these will be included in Q_{vib} as part of the vibrational partition function.
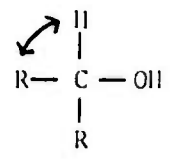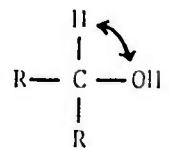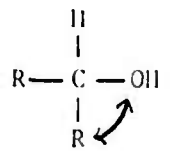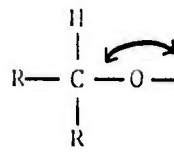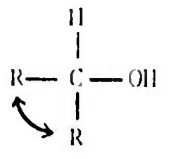
The stretching and bending vibrations appropriate to cellulose, which is a chain molecule of module (H-C-OH), are listed in Tables 1 and 2. Their frequencies differ slightly for molecules containing different isotopes, because the isotopic mass enters into the reduced mass μ of the appropriate oscillator from which the particular frequency is computed, according to:

$$\nu = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{1/2} \tag{4}$$

where K is the force constant of the particular

vibration. Substituting in (3) the frequencies from Table 1, and noting that the torsional frequency, 920 cm⁻¹, is threefold degenerate, one computes $Q(273°K) = 1.2302$ and $Q(298°K) = 1.2981$ for the module {H-C-OH}. In principle, the D-H isotope effect in cellulose involves two possible substitutions: namely, substitution of a

TABLE 2. Bending Vibrations Assumed for Cellulose

Bending Vibration	Bending Frequency, cm⁻¹
H R— C — OH R	920
H R— C — OH R	920
H R— C — OH R	920
H R— C — O — H R	(700)*
H R— C — OH R	(375)

*Herzberg [1945, p. 196, Tables 51 and 89].

†Herzberg [1945, Tables 118 and 119].

TABLE 3. Partition Functions Computed for the Module of Cellulose (H— C —OH) and Its Isotopic Modifications

Partition Function	273°K	298°K
$Q(HCOH)$	1.2302	1.2981
$Q^*(DCOH)$	40.850	52.695
$Q^*(HCOD)$	35.014	28.086
$Q^*(^{13}CH_2O)$	1.4240	1.3511
$Q^*(CH_2{}^{18}O)$	1.5629	1.0059

deuteron for the hydrogen linked to the carbon atom and substitution of the hydrogen attached to oxygen. In the case of R and R' attached to the pivotal carbon, the appropriate reduced mass is insensitive to substitution of H by D because the masses of R and R' are almost infinitely large relative to H or D. The partition functions computed for the various isotopic substitutions of the cellulose module are given in Table 3.

Because of the crudeness inherent in assuming bond frequencies for cellulose to be equal to those known in rather small organic molecules, we neglect anharmonic corrections and complications such as hydration in solution or effect of hydrogen bond formation.

The fractionation ratios can be written as follows. For the oxygen isotopes, there are three equilibriums corresponding to isotopic exchange between cellulose and each of the three oxygen-containing molecules involved in the reaction:

$$^{18}K(O_2) = \frac{Q^*(CH_2{}^{18}O)}{Q(CH_2{}^{16}O)} \frac{Q(^{16}O_2)}{Q^*(^{16}O^{18}O)} \qquad (5a)$$

$$^{18}K(CO_2) = \frac{Q^*(CH_2{}^{18}O)}{Q(CH_2{}^{16}O)} \frac{Q(C^{16}O_2)}{Q^*(C^{16}O^{18}O)} \qquad (5b)$$

$$^{18}K(H_2O) = \frac{Q^*(CH_2{}^{18}O)}{Q(CH_2{}^{16}O)} \frac{Q(H_2{}^{16}O)}{Q^*(H_2{}^{18}O)} \qquad (5c)$$

where Q^* is the partition function for the heavier isotope. For the hydrogen isotopes, two equilibriums enter so that

$$K(HCOD) = \frac{Q^*(HCOD)}{Q(CH_2O)} \frac{Q(H_2O)}{Q^*(HDO)}$$

$$K(DCOH) = \frac{Q^*(DCOH)}{Q(CH_2O)} \frac{Q(H_2O)}{Q^*(HDO)} \qquad (6)$$

and, for the carbon isotopes, only one equilibrium enters, that with CO_2, so that

$$^{13}K = \frac{Q^*(^{13}CH_2O)}{Q(^{12}CH_2O)} \cdot \frac{Q(^{12}CO_2)}{Q^*(^{13}CO_2)} \qquad (7)$$

but what the chemist actually measures [Urey, 1947] is an isotopic fractionation a. For example, for oxygen the fractionation factor corresponding to equation 5a is:

$$\frac{\{2[^{18}O_2] + [^{18}O^{16}O]\}}{\{[^{18}O^{16}O] + 2[^{16}O_2]\}} \frac{[CH_2^{16}O]}{[CH_2^{18}O]} = a^{-1} \qquad (8)$$

Considering the reaction

$$^{18}O_2 + {}^{16}O_2 \leftrightharpoons 2[^{16}O^{18}O] \qquad (9)$$
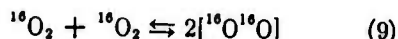
the equilibrium constant is 4, neglecting a tiny correction for isotope effect [Urey, 1947]:

$$4 = [^{16}O^{18}O]^2/[^{18}O_2][^{16}O_2] \qquad (10)$$

because $^{18}O_2$ and $^{16}O_2$, being symmetrical, have only half as many rotational states as the asymmetrical molecule $^{18}O^{16}O$. Substituting (10) into (8), the fractionation factor reduces to

$$a^{18}(O_2) = \frac{Q[^{16}O_2]^{1/2}}{Q^*[^{18}O_2]^{1/2}} \frac{Q^*[CH_2^{18}O]}{Q[CH_2^{16}O]} \qquad (11)$$

Corresponding, $C^{16}O_2$ and $C^{18}O_2$, being symmetric, have only half the rotational states as $C^{18}O^{16}O$, so that

$$a^{18}(CO_2) = \frac{Q[C^{16}O_2]^{1/2}}{Q^*[C^{18}O_2]^{1/2}} \frac{Q^*[CH_2^{18}O]}{Q[CH_2^{16}O]} \qquad (12)$$

but for $a(HCOD)$ and $a(DCOH)$ the isotope

TABLE 4. Partition Function Ratios Computed for Deuterated Cellulose

Partition Function	273°K	298°K
$Q^*[DCOH]/Q[HCOH]^a$	33.206	25.187
$Q^*[HCOD]/Q[HCOH]$	28.462	21.636
$\{Q^*[D_2O]_{gas}/Q[H_2O]_{gas}\}^b$	16.503	12.513
$Q^*[HDO]_{gas}/Q[H_2O]_{gas}$	32.7400	24.9460

The partition function ratio for liquid is obtained by multiplying the partition function ratio for gas by the O/H ratio in liquid divided by that for gas. It is taken here as 1.104 at 273°K, and as 1.074 at 298°K [Merlivat et al., 1963].
^{a}Table 3.
^{b}Urey [1947].

TABLE 5. Partition Function Ratios Computed for Cellulose Containing Heavy Carbon 13

Partition Function	273°K	298°K
$Q^*[^{13}CH_2O]/Q[^{12}CH_2O]^a$	1.1575	1.1435
$\ln Q^*[^{13}CO_2]/Q[^{12}CO_2]$ (gas)^b	0.19732	0.17558
$Q^*[^{13}CO_2]/Q[^{12}CO_2]$ (gas)	1.2181	1.1919

^{a}Table 3.
^{b}Bottinga [1967].

effect is large, so that

$$a(HCOD)$$
$$= \frac{Q^*[HCOD]}{Q[CH_2O]} \left\{ \frac{[2Q[H_2O] + Q[HDO]]}{[Q[HDO] + 2Q[D_2O]]} \right\} \qquad (13)$$

$$a(DCOH)$$
$$= \frac{Q^*[DCOH]}{Q[CH_2O]} \left\{ \frac{2Q[H_2O] + Q[HDO]}{Q[HDO] + 2Q[D_2O]} \right\}$$

Here, while H_2O and D_2O are symmetric, none of the deuterated or hydrogenated cellulose modules are. Finally, because $^{13}CO_2$ and $^{12}CO_2$ have the same number of rotational states, also $H_2^{18}O$ and $H_2^{16}O$, the fractionation factors are

$$a^{18}(H_2O) = \frac{Q(H_2^{16}O)}{Q^*(H_2^{18}O)} \frac{Q^*(CH_2^{18}O)}{Q(CH_2^{16}O)} \qquad (14)$$

$$a^{13} = \frac{Q(^{12}CO_2)}{Q^*(^{13}CO_2)} \frac{Q^*(^{13}CH_2O)}{Q(^{12}CH_2O)} \qquad (15)$$

For the isotope ratios D/H, $^{13}C/^{12}C$, and $^{18}O/^{16}O$, we can now compute the partition function ratios $(Q^*/Q)_{CH_2O}$. The partition function ratios for $(Q^*/Q)_{oxygen}$ are taken from Urey [1947], those for $(H_2O)_{liq}$ are taken from computations of Bottinga [1967] and those for $(CO_2)_{gas}$ from Bottinga [1967] and for HDO and D_2O from Urey [1947].

The ratios appropriate for each isotope exchange are listed in Tables 4, 5, and 6. By substituting these in equations (11) through (15), the fractionation factors have been calculated for 273°K and 298°K. The corresponding temperature coefficients are listed in Table 7.

The temperature coefficient so calculated for $^{13}C/^{12}C$ of 0.36‰/°C, agrees with the coefficient measured for $^{13}C/^{12}C$ in plant and animal material by Sackett and his co-workers [Sackett, et al., 1965; Degens et al., 1968], so that the

TABLE 6. Partition Function Ratios Computed
for Cellulose Containing Heavy Oxygen

Partition Function	273°K	298°K	Source
$Q*[CH_2{}^{18}O]/Q[CH_2{}^{16}O]$	1.2697	1.2833	This paper
$[Q*(^{18}O_2)/Q(^{16}O_2)]_{gas}{}^{1/2}$	1.0923	1.0818	*Urey* [1947]
$\frac{1}{2}\ln\{Q*[C^{18}O_2]_{gas}/Q[C^{16}O_2]_{gas}\}$	0.12530	0.11108	*Bottinga* [1967]
$\{Q*[C^{18}O_2]/Q[C^{16}O_2]\}_{gas}{}^{1/2}$	1.1336	1.1175	
$\ln\{Q*[H_2{}^{18}O]_{gas}/Q[H_2{}^{16}O]_{gas}\}$	0.06822	0.06164	*Bottinga* [1967][a]
$\{Q*[H_2{}^{18}O]/Q[H_2{}^{16}O]\}_{gas}$	1.0706	1.0635	

[a]The partition function ratio for liquid water is obtained by
multiplying the partition function ratio for water vapor with the
$^{18}O/^{16}O$ ratio in liquid water divided by the ratio in the vapor. This
correction is taken as 1.01150 at 273° and as 1.00930 at 298°K [*Bottinga*,
1967, p. 806].

assumption of equilibrium appears to be more
or less valid, and one can hope that the like
calculations for oxygen and hydrogen may be
meaningful.

At equilibrium, the temperature coefficient of
HDO/H_2O is 312‰/°C [*Urey*, 1947], much
larger than that of the (D/H) ratio calculated
for cellulose, so that measuring it in a geographi-
cal distribution of the same kind of trees would
measure the distribution in D/H ratios of rain
water, and measuring it in a chronological se-
quence would measure time dependence of the
rain water.

Our naive assumptions are mainly as follows.
We have assumed that cellulose is formed in
solution, that in cellulose rotations have degen-
erated into torsional vibration, that its vibra-
tions are like those in small organic molecules,
and that manufacture of cellulose in plants is an
almost equilibrium process. (A further assump-
tion has been made in the neglect of acoustical
vibrations of cellulose in the lattice of solid
wood. While these might make a contribution
to the fractionation factors, their temperature
coefficients appear to be negligibly small, judg-
ing from the estimates of *Bottinga* [1967] for
solid calcite; he points out that the lattice con-
tribution to the temperature coefficient is small.
Our main concern in the present paper is with
the magnitudes of the temperature coefficients,

rather than with the fractionation factors them-
selves.)

The intent of the present computation is to
show that all three of the isotope ratios D/H,
$^{13}C/^{12}C$, and $^{18}O/^{16}O$ may well be thermometers,
and that their temperature coefficients may have
measurable magnitudes in bio-organic plant resi-
dues, and so may give information about climate
variation in the past.

For example, we can measure these ratios in a
chronological sequence of tree rings. The results
of *Parker* [1964] are that (1) different plant
species growing side by side in a marine estuary

TABLE 7. Temperature Coefficients Computed
for Isotopes of C, H, and O in Cellulose

Fractionation	273°K	298°K	Temp. Coeff., °/oo/°C
$a^{18}(O_2)$	1.1624	1.1863	+0.96
$a^{18}(CO_2)$	1.1200	1.1484	+1.14
$a^{18}(H_2O)$	1.1725	1.1956	+0.92
a^{13}	0.9503	0.9594	+0.36
a (HCOD)	1.5881	1.5983	+0.4
a (DCOH)	1.8095	1.8606	-2.0

The computed temperature coefficients listed
above agree very well with the value 0.35 °/oo/°C
measured for $^{13}C/^{12}C$ by *Degens et al.* [1968], and
with the value 3.0 °/oo/°C measured for D/H by
Schiegl [1972].

can have different percentages of ^{12}C in total carbon content, and (2) individuals of the same species have about the same percentage of ^{13}C. Therefore, in evaluating past climates from isotope thermometers, we should measure changes in a single species of tree and we should measure a chronological sequence consisting of several individuals, of the same kind of tree, having overlapping life spans. By measuring trees of overlapping life spans, and trees that grow in sparse environments, such as mountain slopes, one may avoid spurious effects caused by the relatively greater removal of CO_2 from air near the ground by abundant low-growing plants.

The temperature coefficient of oxygen in rain water could be as large as $-0.36‰/°C$ [Urey, 1947]. Also important is the fact that CO_2 mixes rapidly through the entire global atmosphere in a time of ~ 5 years, and with the oceans [Bien and Suess, 1967; Suess, 1970; Craig, 1957] in about 15 years, so that at any time the atmospheric carbon isotope ratios reflect the temperature-dependent isotope separation in the sea, which has coefficients of $-0.21‰/°C$ for oxygen [Bottinga and Craig, 1969], and $-0.11‰/°C$ for carbon [Emrich et al., 1970].

One may ask whether there is isotope exchange between the hydrogens bound in old cellulose and in new sap. As Table 1 shows, both hydrogens are bound very tightly, even more so than the C-C bonds, so that, knowing that radiocarbon dates in tree cellulose mainly agree with the tree ring dates, meaning that in heart wood carbon does not exchange, we can hope the same to be true of hydrogen in heart wood. But this point should be tested. When cellulose is prepared in a thin layer or finely ground and repeatedly wetted and dried, there is some exchange [Sepall and Mason, 1961], but these conditions are quite different from those of cellulose in sound heart wood.

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